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THE NATURE OF THE INTERACTION FORCES BETWEEN PARTICLES IN SUSPENSIONS OF GLASS SPHERES IN ORGANIC LIQUID MEDIA[1]

BY P. G. HOWE,[2] D. P. BENTON,[2] AND I. E. PUDDINGTON

ABSTRACT

Electrostatic agglomeration can be induced in suspensions of glass beads in organic liquid media. The stability of the agglomerates is markedly dependent on temperature. The influence of surface roughness and the presence of small quantities of water on the interparticle interaction is discussed. Assuming a simple model the observed relationship between yield value and particle size for systems containing the same concentration of solid phase is derived.

INTRODUCTION

The behavior of suspensions of solids in liquid media is of considerable importance owing to the numerous practical applications of systems of this type which exhibit non-Newtonian behavior. Basically, the behavior of such a system is determined by the interparticle interaction, which is, in turn, determined by the nature and composition of the supporting medium. Suspensions of inert solids in organic liquids have been investigated by a number of workers (5, 12) and the presence of small amounts of water as an immiscible liquid has recently been shown to be of profound importance (9, 10).

Eggleton and Puddington (4) investigated the effect of temperature on suspensions of glass beads in toluene containing various amounts of water. Although the suspensions containing large amounts of water behaved as expected, showing a minimum yield value below the freezing point of water, the anhydrous suspension and that containing 0.1% water showed an unexpected and steady increase in sedimentation volume and yield value as the temperature was lowered to −60° C. This work is concerned with a further investigation of this phenomenon and a consideration of other factors involved in systems of this type.

EXPERIMENTAL

Glass beads, −275 mesh, were supplied by the Flexolite Manufacturing Corporation. The beads were fractionated dry in a current of air by means of an Aminco Roller Particle Size Analyzer. A fraction of average diameter 41 μ

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[2]*N.R.L. Postdoctorate Fellow, 1953–55, National Research Council, Ottawa, Canada.*

was used in all experiments. Fig. 1 shows the distribution of bead sizes. This fraction was selected to conform with that of 43 μ obtained by Eggleton and Puddington by wet fractionation. The main impurity in the beads was a ferromagnetic dust, the bulk of which was removed by flowing the aqueous

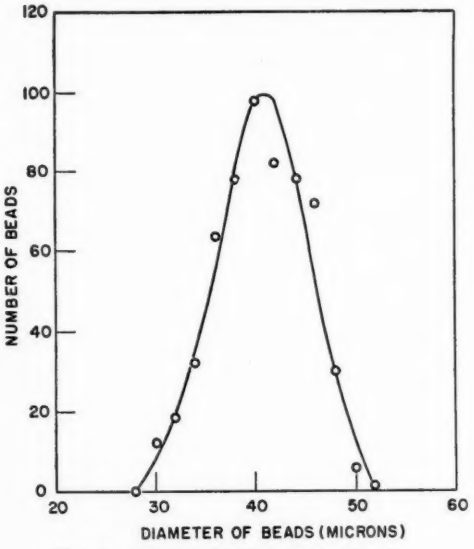

FIG. 1. Size distribution of glass beads.

suspension of beads through a glass tube placed between the poles of a powerful magnet. The beads were then cleaned in aqua regia and extracted with hot distilled water by decantation to remove acid. End washings were strongly alkaline and analysis of the supernatant liquor for Na and Ca showed considerable solution of the soft glass. It is possible that the glass beads used in similar work (4, 13) were considerably etched by solution of the glass. The beads were finally oven-dried before use.

The reagent grade organic liquids were purified as follows. Toluene was dried over calcium hydride and refluxed *in vacuo*. Chloroform was washed several times with distilled water, dried over silica gel, and refluxed *in vacuo*. Methyl alcohol was partially dried over calcium oxide, was distilled into a vacuum reservoir containing magnesium turnings, and after solution of the magnesium was degassed by refluxing *in vacuo*. The required amount of beads was weighed into a calibrated 12 mm. tube attached to the vacuum line. The glass beads were then baked out *in vacuo* at 350° C. until a stick vacuum in the McLeod gauge was obtained, and were allowed to cool. The required organic liquid was then further degassed by repeated distillation between two traps and finally distilled into the tube containing the beads. The tube was then immersed in liquid nitrogen and sealed off at a preformed constriction. A similar tube containing beads with no supporting liquid was also prepared.

Copper spheres, 100–200 mesh, were substituted for the glass spheres in one tube. These were reduced at 350° C. in an atmosphere of hydrogen and the water reaction product was frozen out in a liquid nitrogen trap. The system was then degassed at 350° C. and filled with toluene as described above.

RESULTS AND DISCUSSION

(*a*) *The Behavior of Glass and Copper Spheres in Anhydrous Media*

It was found that the sedimentation volume of the glass beads in toluene was a minimum (the same as for the beads *in vacuo*) and virtually independent of temperature, as long as the suspension was not subjected to too vigorous or sustained agitation. Observations were carried out in an air thermostat capable of regulation to 0.3° C. between room temperature and −60° C. Gentle agitation by inversion of the tube would eventually cause agglomeration and the time required was shortened to a few seconds by vigorous shaking. The maximum sedimentation volume so obtained (about 2 ml./gm. compared with about 0.67 ml./gm. minimum) also appeared to be independent of the temperature, but at room temperature the subsequent collapse of the settled agglomerate to the minimum volume was very rapid, whereas at lower temperatures the agglomerate appeared to be very stable and showed no tendency to collapse over periods of some six hours. Similar behavior was observed for the beads in chloroform but in methyl alcohol no increase in sedimentation volume was observed.

Gallay and Puddington (6) have shown that an attractive force between particles causes an increase in the sedimentation volume by preventing the close packing of the particles. It is apparent from the above observations that the agglomeration observed in the anhydrous toluene and chloroform is caused by the build-up of electrostatic charges which exert a strong attraction between the beads. The formation of the charges is probably owing to the collisions which take place between the beads during agitation or to the relative motion of the glass beads and the supporting liquid. The formation of electrostatic charges by the relative motion of two dielectrics is a well-known phenomenon. It appears that the presence of the liquid phase is important in that it allows for relative motion of the beads with respect to each other or to the liquid medium. The agitation of the glass beads *in vacuo* did not give any agglomeration since there is no resistance to flow.

The reduced copper spheres in anhydrous toluene showed no agglomeration at all from room temperature to −60° C. The resistance of the settled beads measured between two sealed-in tungsten electrodes about 1 cm. apart was less than 1 ohm. This value was obtained immediately after settling and did not alter with time of standing. An adsorbed layer of toluene would be expected to give an appreciably higher resistance since the resistance of the original oxide coated beads was of the order of 5 megohms.

The agglomeration of the glass beads in anhydrous toluene and chloroform and the absence of any such aggregation in anhydrous methanol can be considered in the light of the electrical conductivities of these liquids. Both toluene and chloroform are good dielectrics; toluene has a volume resistivity

of about 10^{-14} ohm-cm. whereas that of methanol is about 10^{-6}. No appreciable adsorption of toluene on glass would be expected but methanol should be chemisorbed and give a suitably conducting surface, thus preventing the formation of localized charge centers during agitation. At room temperature the surface conductance of the glass in toluene is apparently sufficient to cause a rapid collapse of the charged agglomerate.

It is surprising that the agglomerates are so stable at lower temperatures. At contact points the behavior of the liquid can be compared to that of a liquid in a capillary of molecular dimensions. The temperature coefficients of surface resistivity and of liquid viscosity in such a system are not known but are possibly of an order which will explain the observed properties. There is little doubt that adsorption energies and electroviscous forces in such a system are very high compared with normal bulk properties.

The copper beads in toluene showed no agglomeration, and in this case no *localized* charges are capable of existing on the surface of the bead. It should be noted that if the glass beads all possessed a uniform surface charge of the same sign, no agglomeration would be expected since the existence of a uniform surface potential would tend to stabilize a suspension by repulsion between the particles in the same way as an electrical double layer stabilizes aqueous suspensions. The glass beads may, however, possess *localized* surface charges all of the same sign, and agglomerate by electrostatic induction. Alternatively, the beads may possess both positive and negative localized surface charges which would cause the observed flocculation. The existence of a stable charge mosaic on the surface of glass has been suggested elsewhere (3).

The actual mechanism of the electrostatic agglomeration is important in connection with the stabilization of suspensions of inert materials in organic liquid media. Garner and co-workers (7) have shown that an electrical charge is present at the surface of particles of carbon black dispersed in organic liquids and that the particles may be either positive or negative according to the nature of the supporting medium. Toluene was found to give a negatively charged suspension and chloroform a positively charged one. It is possible that this phenomenon and that of the electrostatic agglomeration of the glass beads are related and the same basic phenomenon may cause both stabilization and agglomeration of a suspension according to the nature of the suspended material. When this is sufficiently conductive the charge will distribute itself over the whole surface and stabilization of the suspension will result. The stability of a double layer on a conducting particle of this type may be owing to the seat of the charge not being confined to the periphery of the solid but being smeared out throughout the whole particle. In the case of the glass suspensions, charges may be localized at points on the surface and the adsorption of oppositely charged solvent molecules could take place at other surface locations.

The electrostatic agglomeration of the beads is not affected by small amounts of water although this is more apparent below 0° C., when the water is frozen out on the beads. However, the indication is that the electrostatic behavior is inherent in such suspensions and is not owing to the presence of ionic im-

purities. Suspensions of various materials in organic and aqueous solutions in which the particles are capable of hydrogen bonding with the liquid medium are generally stabilized against flocculation (8). Thus, suspensions of copper sulphide in water and ether are stabilized by the addition of hydrogen sulphide which allows for such bonding to occur. Such bonding would also be expected in suspensions of glass beads in methanol and water and, in fact, these suspensions do not flocculate. However, it might also be expected that in such systems stabilization is brought about by the formation of a continuous double layer on the surface owing to the adsorption of one of the ionic dissociation products of the stabilizing medium.

(*b*) *Minimum Sedimentation Volumes*

The settled volumes of the glass spheres in various liquids are shown in Table I. The minimum volumes are the same in methanol, toluene, water, and

TABLE I

MINIMUM SEDIMENTATION VOLUMES OF GLASS SPHERES IN DIFFERENT LIQUIDS

Supporting medium	Sedimentation volume, ml./gm.		
	Settled under gravity	Tapped down while settling	Centrifuged
Water	0.67	0.67	0.67
Methanol	0.66	0.66	—
Vacuum	—	0.68	—
Toluene	0.67	0.67	—
Chloroform*	0.70	0.70	—

**Higher values in chloroform may be due to small amounts of decomposition products of the chloroform.*

in vacuo indicating that electrostatic agglomeration is absent. In all these cases it is to be noted that the minimum volume is well above that expected for a closest packing of the spheres and since the spheres cover a small but definite fraction range it would be expected that the close packed volume would be still smaller. Table II shows the void fraction for various theoretical types of packing (2) of uniform spheres.

Taking a density of 2.32 for soft glass and 0.67 ml./gm. as the minimum sedimentation volume observed, the calculated porosity is about 0.36. This lies between the orthorhombic and tetragonal-sphenoidal porosities and

TABLE II

THEORETICAL CLOSE PACKING OF PERFECT SPHERES (2)

Packing orientation	Porosity*	Contacts per sphere
Cubic	0.476	6
Orthorhombic	0.395	8
Tetragonal-sphenoidal	0.302	10
Rhombohedral	0.260	12

**Porosity = volume of void space per total volume.*

corresponds to about 9 contacts per sphere compared with the theoretical maximum of 12 contacts per sphere. This may well be the closest packing which can be obtained experimentally but no dilatancy is apparent and there is some evidence that all these suspensions possess a small residual yield value, which would prevent closer packing owing to the force of interaction between the beads. This might be due to a small London – van der Waals interaction between the beads.

(*c*) *The Influence of Water and Surface Roughness*

For suspensions of glass beads in toluene the results of Eggleton and Puddington show that the influence of the electrostatic effect is still apparent in the presence of small amounts of water below a certain concentration. The behavior of the beads with 0.1% water is the same as in the anhydrous suspensions between −60° C. and +30° C., but with 0.28% water only weak electrostatic forces are apparent below 0° C. This is probably owing to the surface roughness of the beads. Preferential adsorption of water would be expected in the surface depressions leaving the surface peaks exposed. Localized charge build-ups would then be able to take place at these peaks. This is in keeping with general electrostatic phenomena.

With 0.28% water the surface depressions will be filled leaving only a few high points exposed. Below 0° C. only weak electrostatic forces are present and the yield value is low. Above 0° C. enough of the surface is covered with water to allow some water necks to form between some of the beads, which causes the yield value to increase sharply. However, the yield value falls off quickly as the temperature is raised owing to the increasing solubility of water in the toluene. The small apparent residual yield value obtained with larger amounts of water below 0° C. might be attributed to a small residual electrostatic effect on a better conducting ice surface or, since surface discontinuities will have been smoothed out by filling the depressions with water, it might also be attributed to increased London – van der Waals forces.

The B.E.T. area of the water-etched beads was shown by Thompson (13) to be as much as 21 times the value for unetched beads. This corresponds to a monolayer coverage by about 0.04% water. At 0.28% water, where coverage is practically complete, about seven monolayers would appear to be sufficient to fill up the surface depressions. Assuming that the volume of the depressions is equal to the volume of the peaks, an approximate mean height of the surface peaks can be estimated as being equal to the thickness of a film of water composed of 14 monolayers, i.e., *ca.* 50 Å. This is probably a low estimate but indicates that the maximum surface irregularities may be of the order of 100 Å.

(*d*) *Yield Value of Suspensions Containing Water*

The high maximum yield value and the large sedimentation volumes of inert suspensions containing water immiscible with the organic liquid medium are owing to the formation of water "necks" between the particles. Bloomquist and Shutt (1) related the sedimentation volumes of glass spheres in various organic liquids to their interfacial tension against water. Those with the largest values gave the largest sedimentation volumes. Kruyt and van Selms (9,

10) found that the yield value of starch and quartz suspensions in organic liquids depended on the care taken in drying the materials and the amount of water subsequently added.

McFarlane and Tabor (11) have shown that the force between a bead and a plate owing to the neck of liquid between them is given by the expression

[1] $$F = 4\pi R\gamma \cos\alpha$$

where F is the force in dynes, R the radius of the bead, γ the interfacial tension, and α the contact angle. The equation applies strictly only for small amounts of water and when the contact angle is very small, but, essentially, for small amounts of water the adhesion is independent of the amount of water in the neck. It has been observed by the present authors that as the water in the neck is increased to large amounts, the adhesion decreases somewhat.

For the adhesion between two spheres the same equation will hold where γ is the interfacial tension between water and the organic liquid. For quartz suspensions Kruyt and van Selms (9, 10) have shown that the yield value is constant over the range 2–12% water and then begins to fall off until the point is reached where the quartz and water separate out as a second phase. This behavior is consistent with that expected for the adhesion between the beads. Below 2% water, where the sigmoid characteristic of the yield value versus water content appears, several factors probably account for the shape of the curve. This could be influenced, for example, by the solubility of water in the organic liquid, the extent of adsorption of water from the organic liquid when below saturation, or the filling of surface discontinuities by water and the consequent continuous increase in neck formation up to the maximum possible.

Kruyt and van Selms also showed that for the same concentration of solid phase the maximum yield value is inversely proportional to the radius of the spheres. They arrived at a relationship between the yield value and the water content of the suspension by calculating the *work* required to separate a pair of glass beads with a known quantity of water in the neck joining them. Eggleton and Puddington noted that the yield value has the dimensions of a force, rather than of work, and that the adhesion between the beads is the important factor.

The observed proportionality between particle size and yield value can be derived by considering the following simple model. Systems in which the interparticle interaction is strong will form a continuous network in the supporting medium composed of chains of particles. The force required to break down this network and cause flow is the yield value of the suspension. Consider an ideal system of uniform spheres which interact strongly when supported in a liquid medium. Let a unit volume of the system contain x chains, each of which is composed of n spheres of radius r. For two such systems containing the same weight of solid but with spheres of radius r_1 and r_2, then the ratio of the total numbers of spheres in the two systems is given by

[2] $$n_1x_1/n_2x_2 = r_2^3/r_1^3.$$

The ratio of the chain lengths is given by

[3] $$n_1 r_1 = n_2 r_2.$$

Combining equations [2] and [3] gives the ratio of the number of chains

[4] $$x_1/x_2 = r_2^2/r_1^2.$$

For any plane of the same area intersecting the volume element the number of chains cutting the plane will be Px where P is some constant allowing for the random orientation of the chains. Therefore, the ratio of the number of chains intersecting such a plane is given by

[5] $$Px_1/Px_2 = r_2^2/r_1^2.$$

The yield value θ is assumed to be proportional to the force across the plane, i.e., the force required to break all the chains intersecting the plane. The force F required to break any one chain will be the force between any two beads in the chain. From equation [1] it is seen that the maximum force between two beads of radius r with a connecting water neck is given by $F = 4\pi r\gamma \cos\alpha$, i.e., $F \propto r$. It follows therefore that

[6] $$\theta_1/\theta_2 = F_1Px_1/F_2Px_2 = r_2/r_1.$$

Thus for the same concentration of solid phase, the yield value is inversely proportional to the radius of the spheres, which is the experimentally observed proportionality.

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THE REACTION OF NITRAMINES WITH HYDROCHLORIC ACID[1]

By A. F. McKay, W. G. Hatton, and M. Skulski

ABSTRACT

A facile process for the conversion of N-(β-nitraminoethyl)-N′-substituted-N″-nitroguanidines into the reactive N-(β-chloroethyl)-N′-substituted-N″-nitroguanidines has been developed. N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine on standing in concentrated hydrochloric acid solution gives a mixture of N-(β-chloroethyl)-N′-phenyl-N″-nitroguanidine and 1-nitro-2-phenylamino-2-imidazoline. N-(β-Chloroethyl)-N′-diethyl-N″-nitroguanidine, which is prepared in a similar manner, is unstable at room temperature and it slowly cyclizes to give 1-nitro-2-diethylamino-2-imidazoline. Some new nitroguanidine derivatives formed from the reaction of amines with methylnitrosonitroguanidine also are described.

It was previously (2) shown that alkyl nitramines in dilute acid solutions decomposed to give alkyl cations. Thus methylnitramine in dilute hydrochloric acid solution gave a 50% yield of methyl chloride from the reaction of the intermediate methyl cation with the chloride ion. The mechanism of this reaction indicated the possibility of substituting the chloro group for a nitramino group in good yield by treating an aliphatic nitramine with an excess of concentrated hydrochloric acid. This assumption was realized (8) with N-β-nitraminoethyl-N′-nitroguanidine on treatment with concentrated hydrochloric acid when a 92.6% yield of the expected N-β-chloroethyl-N′-nitroguanidine was obtained. Since this reaction provided a simple method of obtaining the reactive and highly substituted N-β-chloroethyl-N′-nitroguanidines, it was investigated further.

N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine (I) in concentrated hydrochloric acid solution gave a 74.2% yield of N-(β-chloroethyl)-N′-phenyl-N″-nitroguanidine (III). The filtrate after neutralization in the cold with sodium hydroxide solution gave a 20.4% yield of 1-nitro-2-phenylamino-2-imidazoline (or the tautomeric 1-nitro-2-phenyliminoimidazolidine) (IV). These products are easily explained on the basis of the formation of an intermediate alkyl cation II as shown below. The similarity of the reactions depicted here to those previously outlined for the reaction of acetyl chloride with N-(β-nitraminoethyl)-N′-substituted-N″-nitroguanidines (4, 7, 9, 10) will be apparent. As stressed before (7) the main reason for the complexity ascribed to some of the acetyl chloride – nitramine reactions was the variety of products isolated. Some of these products undoubtedly arose from secondary reactions during the involved isolation procedures. The products from the reaction of the N-(β-nitraminoethyl)-N′-substituted-N″-nitroguanidine with concentrated hydrochloric acid solution can be separated with ease, which eliminates this difficulty.

The structure of N-(β-chloroethyl)-N′-phenyl-N″-nitroguanidine (III) was

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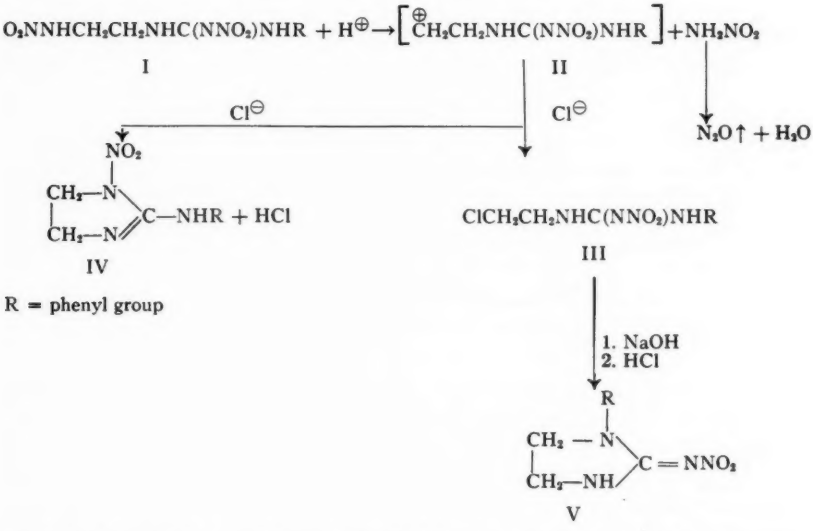
Contribution from Defence Research Chemical Laboratories, Ottawa, Ontario, and L. G. Ryan Research Laboratory of Monsanto Canada Limited, Ville LaSalle, Quebec. Issued as D.R.C.L. Report No. 140.



confirmed by its infrared spectrum and by its conversion to the known 1-phenyl-2-nitriminoimidazolidine (V) (12). 1-Phenyl-2-nitriminoimidazolidine was previously (12) referred to as the tautomeric 1-phenyl-2-nitramino-2-imidazoline. The reason for this change in nomenclature has been discussed recently (13).

A more highly substituted compound N-(β-nitraminoethyl)-N′-diethyl-N″-nitroguanidine also was allowed to stand at room temperature in hydrochloric acid solution. The product from this reaction melted at 96–97° C. and it was identified as N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine by analysis and by its chemical properties. When N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine was heated with water it cyclized to 1-nitro-2-diethylamino-2-imidazoline. The latter compound was isolated as its picrate. On standing in a vial the crystalline N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine changed into a viscous oil with entrained gas bubbles. This oil was dissolved in water and then treated with a saturated solution of picric acid. A 69% yield of 1-nitro-2-diethylamino-2-imidazolinium picrate was obtained. Thus the original crystalline N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine cyclized on standing at room temperature. The presence of gas bubbles in the viscous oil suggests that some decomposition also occurred.

Some new nitroguanidine derivatives have been prepared by the reaction of amines with methylnitrosonitroguanidine (6, 14). These are described in the Experimental section.

EXPERIMENTAL[2]

N-Methyl-N-nitroso-N′-nitroguanidine

This compound (m.p. 118° C. with decomp.) was prepared as previously described (11).

[2]*All melting points were taken on a Kofler block. Microanalyses by Micro-Tech Laboratories, Skokie, Illinois.*

N-Acetyl Ethylenediamine

N-Acetyl ethylenediamine was prepared by the method of Hill and Aspinall (1, 5). Ninety-five per cent ethylenediamine (570 gm., 9.0 moles) was mixed with 264 gm. (3.0 moles) of ethyl acetate and left at room temperature for eight days. The ethyl alcohol and excess amine were removed by distillation *in vacuo*. The residue on distillation *in vacuo* gave 233.3 gm. (69.9%) of N-acetyl ethylenediamine, b.p. 99–103° C. (0.5 mm.). This distillate soon solidified after which it melted at 49.5° C. The melting point given in the literature (5) is 51° C. The residual solid (62.6 gm.) in the distillation flask melted sharply at 173–174.5° C. after one crystallization from 95% ethanol (2.4 cc./gm.). A melting point of 175° C. is given in the literature (5) for N,N′-diacetyl ethylenediamine.

N-(β-Acetylaminoethyl)-N′-nitroguanidine

To 32.7 gm. (0.032 mole) of monoacetylethylenediamine in 35 cc. of water was added portionwise 15.7 gm. (0.0107 mole) of methylnitrosonitroguanidine over a period of 25 min. During the addition period the temperature was held at 22–27° C. A creamy-white solid separated which was removed by filtration and washed with water, yield 11.24 gm. (56.2%). One crystallization from 95% ethanol (9 cc./gm.) raised the melting point from 134° C. to 150.5–151.5° C. Calc. for $C_5H_{11}N_5O_3$: C, 31.75; H, 5.82; N, 37.03%. Found: C, 31.54; H, 5.87; N, 37.28%.

Monocarbethoxyethylenediamine

Monocarbethoxyethylenediamine (b.p. 135–137°C. (23 mm.); ($n_D^{24.8}$ 1.455; $d_4^{24.8}$ 1.029) was prepared in 40% yield by the method of Moore *et al.* (15).

N-(N-Carbethoxy-β-aminoethyl)-N′-nitroguanidine

To 7.5 gm. (0.0568 mole) of monocarbethoxyethylenediamine in 30 cc. of water was added gradually with stirring 2.79 gm. (0.019 mole) of methylnitrosonitroguanidine over a period of 32 min. During the addition period and an additional half hour of stirring, the temperature was held at 30–35° C. The white solid (m.p. 165.0° C.) was removed by filtration and washed with water, yield 3.34 gm. (80.2%). One crystallization from absolute ethanol (44.3 cc./gm.) raised the melting point to 165.5° C. Calc. for $C_6H_{13}N_5O_4$: C, 32.88; H, 5.93; N, 31.96%. Found: C, 33.05; H, 6.22; N, 32.22%.

N-(β-Nitraminoethyl)-N′-diethyl-N″-nitroguanidine

Five grams (0.029 mole) of 1-nitro-2-nitriminoimidazolidine were covered with 20 cc. of diethylamine and then allowed to stand at room temperature for three days. This reaction mixture was acidified and then placed in the refrigerator for two days. The crystals were removed by filtration and washed with ether and ethanol, yield 3.05 gm. (43.1%). Two crystallizations from 95% ethanol raised the melting point from 133–135° C. with decomposition to 152.5° C. with decomposition. The Franchimont test using dimethylaniline was negative. Calc. for $C_7H_{16}N_6O_4$: C, 33.85; H, 6.45; N, 33.85%. Found: C, 33.86; H, 6.48; N, 33.81%.

N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine

N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine (m.p. 139.5–140.5° C.) was prepared in 96% yield as previously described (10).

Reaction of N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine with Hydrochloric Acid Solution

N-(β-Nitraminoethyl)-N′-phenyl-N″-nitroguanidine (4.97 gm., 0.018 mole) was suspended in 10 cc. of concentrated hydrochloric acid solution and left at room temperature for 48 hr. After the reaction mixture was diluted with 10 cc. of water, it was placed in the refrigerator for 12 hr. The crystals (m.p. 101–102° C., resolidified at 112° C. and then decomposed at 160–163° C.) were removed by filtration and washed with water, yield 3.245 gm. (74.2%). Two crystallizations from methanol at room temperature by the addition of water increased the melting point to 112–113° C. with resolidification at 117–118° C. and decomposition at 160–163° C. Calc. for $C_9H_{11}ClN_4O_2$: C, 44.54; H, 4.56; Cl, 14.62; N, 23.09%. Found: C, 44.75; H, 4.65; Cl, 14.92; N, 22.80%. This product possessing a double melting point was further identified as N-(β-chloroethyl)-N′-phenyl-N″-nitroguanidine by cyclization to the known 1-phenyl-2-nitriminoimidazolidine (12). N-(β-Chloroethyl)-N′-phenyl-N″-nitroguanidine (500 mgm., 0.002 mole) was refluxed for one minute with 117 mgm. (0.0027 mole) of potassium hydroxide in 2 cc. of 95% methanol. On cooling, colorless crystals (m.p. 164–168° C.) separated, yield 394 mgm. (92.7%). One crystallization from 95% methanol raised the melting point to 168–168.5° C. The melting point was unchanged on admixture with an authentic sample of 1-phenyl-2-nitriminoimidazolidine (m.p. 168–169° C.).

The mother liquor from the N-(β-chloroethyl)-N′-phenyl-N″-nitroguanidine gave 140 mgm. of the original N-(β-nitraminoethyl)-N′-phenyl-N″-nitroguanidine (m.p. 138–139° C.). The latter compound was identified by a mixed melting point determination with an authentic sample of N-(β-nitraminoethyl)-N′-phenyl-N″-nitroguanidine (m.p. 139.5–140.5° C.).

The original filtrate from the first crop of crystals on neutralization with 10% sodium hydroxide solution gave 602 mgm. (20.45%) of crystals (m.p. 129–130° C.). One crystallization from ethanol raised the melting point to 138–139° C. (m.p. 132.5–133.5° C. by the capillary method). This compound gave a deep green color with dimethylaniline in the Franchimont test (3). Calc. for $C_9H_{10}N_4O_2$: C, 52.42; H, 4.89; N, 27.17%. Found: C, 52.49; H, 4.99; N, 27.00%. This compound gave a picrate (m.p. 146–147° C.) when treated in the usual manner, yield 80.5%. This picrate was identified as 1-nitro-2-phenylamino-2-imidazolinium picrate by a mixed melting point determination with an authentic sample (10).

Reaction of N-(β-Nitraminoethyl)-N′-diethyl-N″-nitroguanidine with Hydrochloric Acid Solution

N-(β-Nitraminoethyl)-N′-diethyl-N″-nitroguanidine (5.0 mgm., 0.020 mole) was covered with 15 cc. of concentrated hydrochloric acid solution and left at room temperature for 19 hr. The clear solution was diluted with one volume of water and then placed in the refrigerator for several hours. During neutral-

ization of the cold solution with 10% sodium hydroxide solution, colorless crystals separated, yield 2.53 gm. (53.51%). Another 534 mgm. (total yield 66.39%) of crystalline material was obtained from the mother liquor on evaporation. The melting point (96–97° C.) of the crude material was not changed by crystallization from absolute methanol. Calc. for $C_7H_{15}ClN_4O_2$: C, 37.76; H, 6.74; Cl, 15.94; N, 25.18%. Found: C, 38.02; H, 6.66; Cl, 16.15; N, 25.00%.

A sample (377 mgm., 0.0015 mole) of this N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine was converted to 1-nitro-2-diethylamino-2-imidazoline by refluxing for 15 min. with 10 cc. of water. The aqueous solution on addition of a saturated aqueous picric acid solution gave a yellow picrate, yield 337 mgm. (47.9%). The picrate melted at 128.5° C. Calc. for $C_{13}H_{17}N_7O_9$: C, 37.58; H, 4.12; N, 23.60%. Found: C, 37.43; H, 4.01; N, 23.20%.

The crystalline N-(β-chloroethyl)-N′-diethyl-N″-nitroguanidine changed into a viscous liquid containing gas bubbles on standing for a few weeks at room temperature. A sample (207 mgm., 0.0009 mole) of this oil gave a 69.9% yield of the picrate melting at 128.5° C. on treatment with an alcoholic solution of picric acid. This picrate did not depress the melting point of the above-described picrate of 1-nitro-2-diethylamino-2-imidazoline.

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THE STRUCTURE OF MONO-*O*-METHYLENE- AND DI-*O*-METHYLENE-D-GLUCOSE[1]

By W. P. Shyluk, John Honeyman, and T. E. Timell

ABSTRACT

The structure of 1,2-*O*-methylene-α-D-glucofuranose has been proved by preparing the 3,5,6-trimethanesulphonate and the 3,5,6-tri-*p*-toluenesulphonate derivatives of this compound from the corresponding derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose. The results also constitute an additional proof for the recently established structure of the 1,2;3,5-di-*O*-methylene-α-D-glucofuranose.

Brownell (1), who was interested in proving the structure of di-*O*-methylene-D-glucose, obtained by its partial hydrolysis a crystalline, non-reducing mono-*O*-methylene-D-glucose. Before his work was completed, however, Schmidt, Distelmaier, and Reinhard (5) established the constitution of the di-*O*-methylene derivative. The present study of the structure of mono-*O*-methylene-D-glucose also confirmed that for the di-*O*-methylene derivative deduced by Schmidt *et al.*

The presence of a furanose ring and the location of the methylene group in the 1,2-position in mono-*O*-methylene-D-glucose were shown by the following reaction sequence. Treatment of 1,2-*O*-isopropylidene-α-D-glucofuranose[2] (I) with methanesulphonyl chloride gave the trimethanesulphonate (II), which had previously been prepared by Helferich and Gnüchtel (2). The isopropylidene group was replaced by a methylene group giving 1,2-*O*-methylene-α-D-glucofuranose 3,5,6-trimethanesulphonate (III), identical with the compound obtained by esterification of mono-*O*-methylene-α-D-glucofuranose (IV). Similarly, 1,2-*O*-isopropylidene-α-D-glucofuranose was converted into 1,2-*O*-methylene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate, also obtained directly from mono-*O*-methylene-D-glucose.

The above results also prove the structure of the di-*O*-methylene-D-glucose. Hough, Jones, and Magson (3) have shown that the hydroxyl group on C_6 is free. Since one methylene group is in the 1,2-position and there is a furanose ring, the second methylene group must be in the 3,5-position.

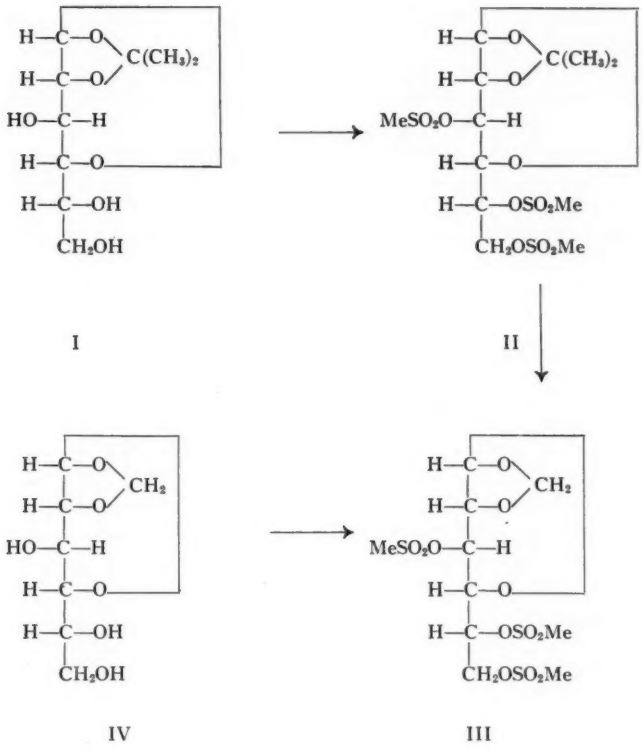
Ohle and Wilcke (4) prepared the 3,5,6-tri-*p*-toluenesulphonate from 1,2-*O*-isopropylidene-α-D-glucofuranose and from its 3-*p*-toluenesulphonate in 15 and 30% yields, respectively. In the present study, preparation of the tri-*p*-toluenesulphonate has been found to present no inherent difficulty, since direct esterification of 1,2-*O*-isopropylidene-α-D-glucofuranose gave the triester in a yield of 82% after one recrystallization from ethanol.

EXPERIMENTAL

1,2;3,5-Di-O-methylene-α-D-glucofuranose

Di-*O*-methylene-D-glucose was obtained by deacetylation with barium methylate in methanol of the di-*O*-methylene-D-glucose 6-acetate, which was

[1]*Manuscript received March 25, 1955.*
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Quebec.
[2]*The more likely α configuration is assumed throughout.*



prepared according to the method of Hough *et al.* (3). The sirup was crystallized and its melting point and specific rotation were identical with those reported by Schmidt *et al.* (5).

1,2-O-Methylene-α-D-glucofuranose

A solution of 1,2;3,5-di-*O*-methylene-α-D-glucofuranose, 13.0 gm., in 2.0% aqueous hydrochloric acid, 175 ml., was kept at 100° C. for one hour, then deacidified by passage through a column of anion exchange resin (Amberlite IR-4B) and evaporated *in vacuo* to 42 ml. The neutral solution was extracted eight times with 70-ml. portions of ethyl acetate and evaporated *in vacuo* to a sirup, 2.73 gm. Glucose was removed by fermentation of its aqueous solution with baker's yeast for 36 hr. at 30° C., after which Super-Cel was added and the mixture was filtered. The clear filtrate was deionized with Amberlite IR-4B and Amberlite IR-120 exchange resins and concentrated *in vacuo* to a sirup, 1.95 gm., which partly crystallized on standing. The crystalline material weighed 0.24 gm. and melted at 145–146° C. Recrystallization from 1.5 ml. of ethanol gave pure 1,2-*O*-methylene-α-D-glucofuranose, m.p. 147–148° C., $[\alpha]_D^{22}$ −6.2° (*c*, 1.2 in water). Calc. for $C_7H_{12}O_6$: C, 43.8; H, 6.30%. Found:

C, 43.7; H, 6.21%. The material was non-reducing to the copper reagent of Shaffer and Somogyi (6).

Crude di-*O*-methylene-D-glucose, 6.8 gm., was recovered by evaporation of the first four ethyl acetate extracts. The other four extracts were evaporated *in vacuo* to a sirup, 3.6 gm., which was dissolved in 10 ml. of water and extracted twice with 10-ml. portions of ethyl acetate. The glucose was removed by fermentation and the solution evaporated to a sirup, which was dissolved in a small amount of ethanol and seeded with pure 1,2-*O*-methylene-α-D-glucofuranose, crystallization occurring slowly at room temperature. The crude material was recrystallized from ethanol to yield 0.09 gm. of 1,2-*O*-methylene-α-D-glucofuranose, m.p. 147–148° C. The total yield of the mono-*O*-methylene-D-glucose was 0.34 gm. or 5.8% of theory.

1,2-O-Isopropylidene-α-D-glucofuranose 3,5,6-Trimethanesulphonate

Monoacetone glucose, 4.4 gm., was dissolved in 9 ml. of pyridine with slight heating, after which methanesulphonyl chloride, 5.5 ml., was added and the mixture cooled while shaking. After 42 hr. at room temperature a few drops of water were added to the reaction mixture followed after 15 min. by a few more drops. An additional amount of water, 30 ml., was added after some time, at which point the sirup crystallized while the mixture was being stirred. The crude product amounted to 8.0 gm., corresponding to a yield of 90.5%. The material was recrystallized twice from chloroform and *n*-pentane at room temperature to give 6.3 gm. of 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-trimethanesulphonate, m.p. 162.5–163.5° C., $[\alpha]_D^{22}$ −20.4° (*c*, 1.8 in pyridine). Helferich and Gnüchtel report m.p. 165° C., $[\alpha]_D$ −24.2° in pyridine for this compound.

1,2-O-Isopropylidene-α-D-glucofuranose 3,5,6-Tri-p-toluenesulphonate

Monoacetone glucose, 4.4 gm., was dissolved in 10 ml. of pyridine and 16 gm. of *p*-toluenesulphonyl chloride was added gradually while cooling, after which the mixture was kept at room temperature for four days. Water was added dropwise with cooling and stirring; the thick sirup crystallized while being ground in a mortar with more water. The crystals were collected and washed with water. The crude product weighed 14.1 gm., m.p. 118–123° C. Recrystallization from ethanol at room temperature gave 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate, 11.1 gm., in 81.6% yield, m.p. 129–130° C., $[\alpha]_D^{22}$ −4.3° (*c*, 1.4 in chloroform). Ohle and Wilcke (4) report m.p. 129° C., $[\alpha]_D$ −5.4° in chloroform for this compound.

Conversion of 1,2-O-Isopropylidene-α-D-glucofuranose 3,5,6-Trimethanesulphonate into the Methylene Analogue

Paraformaldehyde, 2.75 gm., and 1,2-*O*-isopropylidene-α-D-glucofuranose trimethanesulphonate, 2.5 gm., were dissolved in 10 ml. of glacial acetic acid by heating on a steam bath. Concentrated sulphuric acid, 0.75 ml., was slowly added and the reaction mixture kept on a steam bath for 80 min. Water, 20 ml., was added to the cooled reaction mixture, which was subsequently extracted twice with 20-ml. portions of chloroform. The combined chloroform solut-

ions were washed with 20 ml. of water, then another 20-ml. portion of water, to which solid sodium bicarbonate was added until no more reaction was evident. After further washing with two 20-ml. portions of saturated aqueous sodium bicarbonate and three 20-ml. portions of water, the chloroform solution was dried over anhydrous sodium sulphate and concentrated *in vacuo* at 50°C. to a partially crystallized sirup. Crystallization from chloroform and *n*-pentane gave 1,2-*O*-methylene-α-D-glucofuranose 3,5,6-trimethanesulphonate, 1.4 gm. in 60% yield, m.p. 92.5–100° C. Two more recrystallizations from the same solvents yielded 0.8 gm. of a pure product, m.p. 104.5–105.5° C., $[\alpha]_D^{22}$ −13.4° (*c*, 1.4 in pyridine). Calc. for $C_{10}H_{18}O_{12}S_3$: C, 28.3; H, 4.24%. Found: C, 27.8; H, 4.18%.

Conversion of 1,2-O-Isopropylidene-α-D-glucofuranose 3,5,6-Tri-p-toluenesulphonate into the Methylene Analogue

Paraformaldehyde, 2.75 gm., and 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate, 2.5 gm., were suspended in 10 ml. of glacial acetic acid and the mixture cooled in an ice-bath. Concentrated sulphuric acid, 0.75 ml., was slowly added and the mixture was kept on a steam bath for 80 min. The product was isolated as described for the trimethanesulphonate and amounted to 2.1 gm. in 84% yield, m.p. 120–128° C. after one recrystallization from chloroform and *n*-pentane at room temperature. Two more recrystallizations from the same solvents gave 0.8 gm. of 1,2-*O*-methylene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate, m.p. 134.5–135° C., $[\alpha]_D^{22}$ +9.8° (*c*, 1.2 in chloroform). Calc. for $C_{28}H_{30}O_{12}S_3$: C, 51.4; H, 4.59%. Found: C, 51.3; H, 4.47%.

1,2-O-Methylene-α-D-glucofuranose 3,5,6-Trimethanesulphonate

Methanesulphonyl chloride, 0.2 ml., was added to a solution of 0.152 gm. of 1,2-*O*-methylene-α-D-glucofuranose in 0.32 ml. of pyridine and the mixture was kept at room temperature for 40 hr. Excess mesyl chloride was decomposed by addition of a few drops of water. After the addition of 2 ml. of water, the sirup crystallized while being stirred; the solid, after washing with two 2-ml. portions of water, amounted to 0.32 gm. Two recrystallizations from chloroform and *n*-pentane at room temperature gave 1,2-*O*-methylene-α-D-glucofuranose 3,5,6-trimethanesulphonate, 0.16 gm., m.p. 106–107° C., $[\alpha]_D^{22}$ −12.8° (*c*, 1.3 in pyridine). No depression of melting point was detected when this material was mixed with the product from the replacement of the isopropylidene by a methylene group in 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-trimethanesulphonate.

1,2-O-Methylene-α-D-glucofuranose 3,5,6-Tri-p-toluenesulphonate

p-Toluenesulphonyl chloride, 0.55 gm., was slowly added to a solution of 1,2-*O*-methylene-α-D-glucofuranose, 0.15 gm., in 0.35 ml. of pyridine. The solution was allowed to stand at room temperature for three days, after which a few drops of water were added to decompose the excess tosyl chloride. The sirup was stirred with 2.5 ml. of water and the crystals formed were separated and again treated with 2.5 ml. of water. The crude product, 0.50 gm., was recrystallized twice from chloroform and *n*-pentane to yield 0.18 gm. of

1,2-*O*-methylene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate, m.p. 135.5–136° C., $[\alpha]_D^{22}$ +10.0° (*c*, 1.4 in chloroform). No depression of the melting point was noted when this material was mixed with the product from the replacement of the isopropylidene group by a methylene group in 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-tri-*p*-toluenesulphonate.

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REACTIONS OF ARYLSULPHONIC ESTERS

II. THE ALKYL GROUP[1]

By P. M. Laughton[2] and R. E. Robertson

ABSTRACT

As part of the project outlined in Paper I of this series, we report kinetic data, including Arrhenius parameters, for the solvolysis of a number of alkyl benzene- and toluene-sulphonates in ethanol and in water. The alkyl groups include the α- and β-methylation series: methyl, ethyl, isopropyl, *n*-propyl, isobutyl, and neopentyl; the straight chain series *n*-butyl and *n*-amyl; and a small group of oxygen-containing chains. The observed rates for the α-methylation series parallel those for the bromides and nitrates, and for the β-methylation, those for the bromides. However, it is evident that current interpretations of rate differences observed in the straight chain and oxygenated series cannot be applied with confidence to the benzenesulphonates since the changes in the Arrhenius parameters are larger than the observed differences in the rate.

In connection with our survey of the behavior of alkyl arylsulphonates in solvolysis, we have examined the effect of changing the structure of the alkyl group. Since this work was undertaken, Winstein's laboratory has reported data on many alkyl groups, mostly in acetic acid and in formic acid and from the point of view of rearrangements. Our work is chiefly concerned with nucleophilic solvents—water and alcohols—and with less complicated alkyl groups.

In particular we hope to be able to characterize the system

$$ROH + ArSO_3R' \rightarrow R{-}O{-}R' + ArSO_3H$$

sufficiently comprehensively that our data may be used in an attack on the problem of the detailed picture of solvent participation in this apparently very simple reaction.

The analysis of the mechanism of displacement reactions has reached a point where most of the large rate-controlling effects have yielded to a semi-quantitative treatment. Hammett's (17) free energy relationship, $\log k/k^\circ = \rho\sigma$, where σ is a measure of the relative effect of substituents in rigid molecules, has recently been extended by Swain (33) to some nucleophilic displacement reactions in the aliphatic series, $\log k/k^\circ = sn$, where s is a measure of the sensitivity of substrate to the nucleophility of the attacking agent. Swain also points out that this equation and that of Winstein, Grunwald, and Jones (39) $\log k/k^\circ = Ym$ (where Y = "solvent ionizing power") may both be special cases of the more general case, $\log k/k^\circ = sn + s'e$, where s' is a measure of substrate sensitivity to electrophilicity in a generalized termolecular displacement. Even the very difficult problem of steric effects seems to be approaching quantitative treatment (cf. Dostrovsky, Hughes, and Ingold (10); Newman (26); Brown (4); Taft (35), among many others).

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This leaves as a major unknown variable the problem of the detailed participation of the medium. While an approach to this problem can be made by considering the solvent as a bulk dielectric, this can only be a first approximation. Taft (34) and Evans and Hamann (13) have interpreted relative rates using the concept of interference with solvation by groups about the reaction site. Yet, as Swain (33) comments, few precise kinetic data are available for treating the effect of different solvents on relative rates of substrates. A further complication is that most of the data available, for solubility reasons, are in a variety of mixed solvent systems. Also, much of the work has been reported at single temperatures because, in the words of Ingold (19, pp. 255–56), as "kinetic effects become smaller, the first quantity to show unintelligible irregularities is the Arrhenius energy of activation".

While we are by no means certain what lines of attack will solve the problem of solvent participation, we hope that our consistent body of kinetic data may provide information useful in this respect. We are certainly going to exercise due caution about attaching any simple significance to small differences in activation energy (19); however, we are sanguine enough to provide temperature coefficients in the hope that what we cannot ourselves interpret may prove useful to others.

RESULTS AND DISCUSSION

α-Methylation Series

The survey reported here covers a number of alkyl groups of recurring interest in other systems. Since this work was undertaken, two communications from Tommila's laboratory have appeared, dealing with some of these systems (37, 38). Table I shows relative rates and Arrhenius parameters ($k = pZ\,e^{-E_A/RT}$) for the series of increasing α-methylation in ethanol and water. (We also (11, 37) have found *t*-butyl sulphonates too unstable for isolation.) This series shows the minimum at the ethyl compound to be expected (19, pp. 317–18) for a shift in mechanistic category from S_N2 toward S_N1. It is noteworthy that the increased rate for the isopropyl derivative in both solvents is due to a more favorable entropy term which outweighs an increase in activation energy. One factor which should result in a more positive entropy for isopropyl is the probability that the solvent is more highly ordered about the initial state, in which ionic contributions to the structure are favored. This increase would, however, have to be larger than any corresponding change in ordering about the more nearly ionized transition state.

In water the anticipated shift towards S_N1 is apparent, the ethyl compound drawing up to the methyl, and isopropyl greatly increasing.[3] These relationships are dealt with in detail in the previous paper in this series (28) in which the benzenesulphonates are compared with the bromides and the nitrates.

β-Methylation Series

The second series of wide interest is that of β-methylation. Table II records

[3]*That the solvolysis of the primary esters must be stereochemically S_N2 is, however, established by the elegant work of Streitwieser on active butanol-1-d p-Br benzenesulphonate (J. Am. Chem. Soc. 77: 1117. 1955).*

our data in ethanol and water for the series ethyl, *n*-propyl, isobutyl, and neopentyl.

TABLE I

SOLVOLYTIC RATE CONSTANTS FOR THE REACTION OF BENZENESULPHONATES WITH ETHANOL AND WATER

$C_6H_5SO_3R + R'OH$; R′ = ethyl, 0.01 *M*; R′ = H, 0.2 gm./l.

R′	R	*T*, °C.	$k \times 10^5$ sec.$^{-1}$	E_A, kcal./mole*	$\log_{10} pZ$
Et	Me	70.00	7.04 ± 0.03		
		80.00	16.73 ± 0.09	20.40 ± 0.45	8.847
		90.00	36.6 ± 0.3		
	Et	70.00	3.06 ± 0.02		
		80.00	7.53 ± 0.03	21.38 ± 0.27	9.107
		90.00	17.22 ± 0.10		
	*i*Pr	50.00	1.262 ± 0.012		
		60.00	3.71 ± 0.04	22.95 ± 0.12	10.627
		70.10	10.24 ± 0.08		
H	Me	50.003	19.66 ± 0.08		
		60.026	52.66 ± 0.13	20.52 ± 0.47	10.181
		74.906	193.4 ± 0.4		
	Et	50.125	18.99 ± 0.12		
		60.026	50.11 ± 0.10	21.04 ± 0.06	10.500
		74.892	195.2 ± 0.2		
	*i*Pr	0.092	1.952 ± 0.008		
		20.010	34.58 ± 0.03	22.78 ± 0.42	13.513
		30.122	124.3 ± 0.6		
		50	(1270)		

**The "errors" reported for the Arrhenius energies of activation may be partially attributed to the ΔC_p of activation for these systems, which is of the order of 30 cal./mole degree in water (29). For example, such a C_p would be equivalent to a curvature of ±0.4 kcal./mole for a 25° range. Known or estimated ΔC_p's are capable of accounting for most of the small discrepancies between our work and the Arrhenius parameters recently reported by Tommila et al. (37, 38).*

TABLE II

SOLVOLYTIC RATE CONSTANTS FOR THE REACTION OF ALKYL BENZENESULPHONATES WITH ETHANOL AND WATER

$C_6H_5SO_3R + R'OH$; R′ = ethyl, 0.01 *M*; R′ = H, 0.2–0.05 gm./l.

R′	R	*T*, ° C.	$k \times 10^5$ sec.$^{-1}$	E_A	$\log_{10} pZ$
Et	Et	80.00	7.60	21.38	9.107
	Pr	50.00	0.248 ± 0.003		
		80.00	4.41 ± 0.05	21.45 ± 0.60	8.906
		90.00	9.84 ± 0.09		
	*i*Bu	50.00	0.0178 ± 0.0005		
		80.00	0.383 ± 0.004	23.16 ± 0.03	8.918
		90.00	0.949 ± 0.011		
	NeoPen*	110.0	0.0984 ± 0.0014		
		120.0	0.255 ± 0.008	28.50	10.260
		80.00	(0.0043)**		
H	Et	60.026	50.1	21.04	10.500
	Pr	50.125	13.09 ± 0.09		
		60.026	35.59 ± 0.11	21.09 ± 0.37	10.376
		74.953	135.9 ± 0.3		
	*i*Bu	59.989	11.75 ± 0.07		
		74.902	55.40 ± 0.06	23.67 ± 0.40	11.60
		83.926	129.1 ± 0.6		
	NeoPen	59.998	5.48 ± 0.04		
		74.900	26.8 ± 0.02	24.98 ± 0.45	12.13
		83.932	68.8 ± 0.7		

**Tosylate.* ***Extrapolated.*

In alcohol we see again the slight jump of about 1 kcal./mole in activation energy for the isobutyl derivative, followed by the large jump of 7 kcal./mole for the neopentyl compound, as noted before in the case of the bromides (10).

Winstein (40, 41) shows that changing the solvent from ethanol through acetic acid to formic acid steadily increases the rate of neopentyl tosylate, indicating a cationic intermediate in all three. He also presents evidence for some anchimeric participation by the β-methyls. This probable difference in mechanism together with the possibility that solvent may assist the ionization by an attack on the β-carbon discourages detailed speculation about the rise in the entropy factor. The possible explanation for the similar increase with isopropyl, based on a more polar initial state, is not available for this compound.

The neopentyl tosylate was prepared in order to check the data of Winstein (40, 41) but the benzenesulphonate was used for the work in water because of solubility difficulties. Winstein's value for the solvolysis of neopentyl tosylate in alcohol touches our two-temperature Arrhenius plot, although his extrapolated value at 75° implies a somewhat different activation energy.

The relative rates for our series in water at 60° (Me: Et: *i*Bu: NeoPen: :10: 9.6: 2.2: 1.0) are similar to the corresponding series for the tosylates in acetic acid (10: 9.1: 2.8: 1) although there is a difference in rate between the two series of more than three powers of ten. Since there is also a difference in the range of activation energies (9 kcal./mole in acetic acid and $4\frac{1}{2}$ kcal./mole in water) one must recognize that the similarity in relative rate sequences here results from fortuitous choice of temperatures for comparison.

Straight-chain Series

Because of the appearance, among the more usual monotonously decreasing rate series (13; 19, p. 319), of the occasional report of straight-chain anomalies in the butyl–pentyl region, we have also examined the series: methyl, ethyl, propyl, butyl, and pentyl in both ethanol and water. Data are recorded in Tables III and IV. Adsorption effects, which begin to become important at very low solubilities (*ca.* 0.0002 *M* for the pentyl compound), have impeded an extension of the series in water. *n*-Hexyl benzenesulphonate in water, on the basis of less precise data, (judging from scatter in the Guggenheim rate plots) solvolyzes more slowly than *n*-pentyl.

There is a minimum rate at propyl in water, but the differences both in rates and in activation parameters are very small. We have no explanation for this minimum which could be generalized for other cases, some of which show peculiar fluctuations.

For example, the following orders of reactivity may be found in the literature for primary amines: Me > Et < Pr < Bu < Pen (5); Me < Et > Pr < Bu < Pen (5); Me > Et > Pr < Bu > Pen (1, 22). Brown (5) has suggested that a break in the series should occur for the first member for which the free rotation of the end of the chain is reduced or increased by changes at the reaction site in the product or transition state. This concept by itself implies

TABLE III

SOLVOLYTIC RATE CONSTANTS FOR THE REACTION OF ALKYL BENZENESULPHONATES IN DRY ETHANOL, 0.01 *M*

R	*T*, ° C.	$k \times 10^5$ sec.$^{-1}$	E_A	$\log_{10}pZ$
Me*	80.00	16.7	20.40	8.847
Et*	80.00	7.60	21.38	9.107
Pr**	80.00	4.41	21.45	8.906
Bu	80.00	4.23 ± 0.04		
	90.00	9.06 ± 0.08	20.98	8.611
	100.00	21.0 ± 0.3		
Pen	77.42	3.70 ± 0.03		
	79.97	4.07 ± 0.11	21.56 ± 0.80	8.954
	90.00	10.8 ± 0.2		
	100.00	22.5 ± 0.6		
$EtO(CH_2)_2$***	100.00	3.88 ± 0.06		
	105	5.46 ± 0.06	19.62 ± 0.37	7.081
	110	7.79 ± 0.05		
$EtO(CH_2)_3$***	90.00	4.20 ± 0.07		
	(100)	(8.61)	21.07	8.277
	105.00	1.254 ± 0.006		
	110.0	17.9 ± 0.3		
$(EtO)_2C(CH_2)_2$***	100.00	6.35 ± 0.05		
	110.00	12.49 ± 0.08	19.74 ± 0.65	7.366
	119.9	24.4 ± 0.4		
$NC(CH_2)_2$***	99.9	1.28 ± 0.01	(21)	(7.5)
	110.0	2.72 ± 0.03		

**From Table I.* ***From Table II.* ****p-Toluenesulphonate.*

TABLE IV

SOLVOLYTIC RATE DATA FOR THE REACTION OF ALKYL BENZENESULPHONATES IN WATER, 0.2 GM./L. OR LESS

R	*T*, ° C.	$k \times 10^5$ sec.$^{-1}$	E_A	$\log_{10}pZ$
Me	50.003	19.66	20.52	10.181
Et	50.125	18.99	21.04	10.500
Pr	50.00	23.09	21.09	10.376
Bu	39.869	5.09 ± 0.04		
	49.904	14.38 ± 0.04	20.53 ± 0.30	10.040
	60.026	37.5 ± 0.5		
Pen	39.870	5.275 ± 0.007		
	50.125	15.6 ± 0.3	20.70 ± 0.60	10.173
	60.026	39.5 ± 0.4		
Hex	49.991	15.23 ± 0.07		
$MeO(CH_2)_2$	50.009	0.9095 ± 0.00		
	59.993	2.610 ± 0.00	22.84 ± 0.23	10.399
	74.901	11.58 ± 0.05		
$EtO(CH_2)_2$	50.009	0.966 ± 0.006		
	60.173	2.69 ± 0.05	22.45 ± 0.77	10.149
	74.900	11.77 ± 0.07		
$EtO(CH_2)_3$	49.904	3.636 ± 0.014		
	60.026	10.18 ± 0.16	21.93 ± 0.17	10.396
	74.900	42.30 ± 0.46		

a vertical displacement at the critical chain length in an otherwise monotonously increasing or decreasing series, an effect which seems intuitively reasonable although its order of magnitude is difficult to evaluate, especially in a condensed phase. However, this cannot be the whole story where the series passes through a minimum as it does in the case of Table IV, or where the curve has a zig-zag character (13).

Anomalies similar to our own have been reported for displacements by ions. Segaller's (31) results for the displacement of alcoholic phenoxide on alkyl iodides show a dip at pentyl. Crowell's (9) work on the attack of alcoholic thiocyanate on alkyl bromides shows a rise to octyl from a minimum at butyl. McKay (23) also found a minimum at butyl for the iodide exchange reaction, pentyl being slightly faster than propyl. On the other hand, the data of Conant and Hussey (6) for iodide displacement on chlorides in acetone show upward displacements in a decreasing curve at pentyl and octyl.

Oxygen-containing Alkyl Groups

Because of the peculiarity reported by Rabinovitch and Schramm (27) for the alkaline hydrolysis in aqueous acetone of β-ethoxyethyl acetate (k_2 twice that for ethyl acetate, but E_A 15.4 kcal./mole versus 11.7 for the ethyl ester), we examined several β- and γ-substituted derivatives in alcohol.[4] All three compounds, β-ethoxyethyl, γ-ethoxypropyl, and β-carbethoxyethyl *p*-toluenesulphonate were an order of magnitude *less* reactive than the simple alkyl esters. (The β-chloroethyl and β-cyanoethyl compounds also reacted very slowly, but the second functional group in each reacted at comparable rates.) However, the activation energies are slightly lower than others in the series, the drop in rate arising from the entropy factor.

This decrease in rate corresponds to that noted for solvolysis of β-ethoxyethyl chloride in aqueous dioxane versus butyl (2), and the very slow solvolysis of β-ethoxyethyl iodide in water (21) as compared with ethyl iodide. In this latter note (21) and in an earlier paper from the same laboratory (8), the suggestion made by Hinshelwood, Laidler, and Timm (18) is used to relate the polar effect of substituents on the heat of activation in displacement reactions. Although this relation should hold only for ΔH_A^0, not for ΔH_A^T, these authors base their discussion on a value of E_A for methyl iodide in water, a reaction which has the large ΔC_p of -67 cal./mole degree (15), and one for ethyl iodide which is in doubt because of a side reaction (25). Further, they assume that the only changes in E_A that are significant arise from polar effects of the substituents, although whatever changes in the ordering of solvent are responsible for the large changes in $\Delta S^{\ddagger}$ must surely make substantial concomitant contributions to E_A.

Although both electron-releasing (12, 14) and electron-withdrawing (3) substituents may facilitate S_N2 displacements by anions, evidently those involving neutral molecules are hindered by electron-withdrawing groups. One might expect the electrophilicity of the carbon undergoing substitution to be more important for the weaker nucleophilics.

EXPERIMENTAL

Materials

Properties of the esters are given in Table V. Methyl and ethyl benzenesulphonate were purified as used by fractional freezing of Eastman Kodak

[4]*We later became aware of the paper by Salmi and Leimu (30) reporting data for the acetates and a number of other esters in pure water and aqueous dioxane. In both solvents the rate of the Cellosolve esters is again roughly twice that of the ethyl esters, but activation energies calculated from their rates are only about 1 kcal./mole higher for the β-ethoxyethyl esters.*

TABLE V

PROPERTIES OF BENZENESULPHONIC ESTERS

Ester	n_D^{25}	N.E.	Analysis obtained		Calculated	
			%C	%H	%C	%H
Pr *p*-H[a]	1.5035	202.2				
Bu *p*-H[b]	1.4998	215.6				
*i*Bu	1.4962	214.7	56.15	6.55	56.05	6.59
Pen *p*-H[b]	1.4987	229.7				
NeoPen *p*-H[a]	1.4932	227.3	57.95	6.95	57.87	7.06
Hex *p*-H[b]	1.4945	244				
$MeO(CH_2)_2$ *p*-H	1.5072	218.7	50.12	5.16	49.99	5.59
$EtO(CH_2)_2$ *p*-H[a]	1.5009	231.2	52.17	6.11	52.16	6.13
$EtO(CH_2)_3$ *p*-H	1.4962	243.0	53.95	6.55	54.08	6.60
$EtO(CH_2)_2$ *p*-Me[a]	1.5039 (26° C.)	246	m.p. 15–16° C.			
$EtO(CH_2)_3$ *p*-Me	1.4960 (27° C.)	253	55.88	7.06	55.78	7.05
$EtO_2(CH_2)_2$ *p*-Me[a]	1.5011 (28° C.)	solidifying and decomposing on standing				
$NC(CH_2)_2$ *p*-Me[a]	m.p. 64.0–64.5° C.					
NeoPen *p*-Me[c]	m.p. 47.0–48.0° C.	243	59.50	7.34	59.48	7.49

[a]*Ref. 32.* [b]*Ref. 11.* [c]*Ref. 41.*

white label material. β-Cyanoethyl and β-ethoxycarbonylethyl *p*-toluenesulphonate were prepared according to the published methods (32). The remaining esters were synthesized by the Tipson method (36) using the appropriate alcohols. Of the alcohols, propyl, isopropyl, butyl, isobutyl, methoxyethyl, ethoxyethyl, β-cyanoethyl, and β-chloroethyl were refractionated from the best available commercial products. All liquid esters were repurified before each series of runs by redistillation from a molecular still, giving colorless products.

γ-Ethoxypropyl alcohol was prepared by reduction of refractionated Eastman Kodak β-ethoxypropionaldehyde with either lithium aluminum hydride or hydrogen and Raney nickel catalyst. After fractionation under reduced pressure its properties correspond to those given by Karvonen (20). The alkoxyalkanols were redistilled just before use because of peroxide formation.

Since analytical grade *n*-pentyl alcohol proved to be a mixture on fractionation, both it and neopentyl alcohol were prepared by Grignard reactions with formaldehyde (7), using *n*-butyl bromide and *t*-butyl chloride respectively.

n-Hexyl alcohol, d_{20}^{20} 0.8178, n_D^{20} 1.4159, was purified from Eastman Kodak practical grade by repeated recrystallization of the *p*-hydroxybenzoate, m.p. 52.0–2.8°, (from petroleum ether) followed by saponification and fractionation.[5]

Ethanol was purified by distillation from sodium and diethyl phthalate (24). Conductance water was prepared by passing distilled water through an Amberlite MB-1 mixed bed resin.

Methods

The work in alcohol as a solvent was done as described in Paper I (28).

In water, rates were followed by conductance methods to be described in Paper III of this series. The Guggenheim method of treatment of data was

[5]*This purification was carried out by Mr. A. Rayner of Carleton College.*

used (16). Precisions recorded in the tables are within runs for the work in ethanol and between runs for the work in water.

For the work in alcohol, temperature was controlled to ±0.01–0.02 C.° using tenth degree thermometers calibrated by the Heat Section of the Division of Physics. For the conductance work, temperature was controlled to ±0.001–0.003 C.°, measured by a platinum resistance thermometer and a Leeds and Northrup G-1 Mueller bridge.

We were initially disturbed by the fact that ethyl benzenesulphonate in water gave a consistently higher value by conductance than by titration according to Tommila's procedure (38). However, there appeared to be appreciable hydrolysis of the ester during the titration. Accordingly, we carried out a titration run in an early model of a continuous titration device. This result confirmed that obtained by conductance. Except for the least soluble esters, adsorption did not appear to interfere with the conductance measurements, since results were indistinguishable for the variety of sizes and shapes of cells which were used in many of the runs. For the *n*-butyl and the pentyl esters, cells with small surface to volume ratios had to be used.

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A NEW METHOD FOR THE PREPARATION OF D-ERYTHROSE AND OF L-GLYCERALDEHYDE[1]

By A. S. Perlin and Carol Brice

ABSTRACT

D-Glucose is degraded selectively to di-*O*-formyl-D-erythrose by oxidation with two moles of lead tetraacetate. The ester groups are easily hydrolyzed, giving D-erythrose in an over-all yield of at least 80% of theory. In like manner oxidation of L-arabinose, followed by hydrolysis, affords L-glyceraldehyde. It is suggested that D-erythrose can readily associate intermolecularly, a property previously ascribed among sugars only to the trioses.

INTRODUCTION

Among monosaccharides the tetroses constitute probably the most poorly characterized group. Only one preparation of a crystalline tetrose, that of D-threose, has been reported (6), but subsequent investigations by Hockett (9, 10) and Hockett *et al.* (11) have cast serious doubt on the identity of this preparation. The current importance of the tetroses is illustrated by the use of D-erythrose as a starting point for synthesis of 2-deoxy-D-ribose (20, 29) and of ribose-1-C^{14} (7, 18).

At least seven methods for preparing D-erythrose are recorded in the literature. Five of these have been evaluated by Overend, Stacey, and Wiggins (20), who recommended the Ruff procedure (26) as modified by Hockett and Hudson (12), and two additional methods have since been reported (30, 25, 16, 14). All of these procedures involve degradation of an appropriate sugar derivative—the acid, glucal, acetal, or mercaptal—which, however, is itself sometimes not obtained readily or in good yield. This communication now reports a convenient preparation of D-erythrose in high yield directly from D-glucose.

When aldohexoses are treated with lead tetraacetate they rapidly consume two moles of oxidant, after which the reaction becomes very slow (13, 24). Applied to D-glucose it is found that the initial rapid stage of the reaction corresponds to virtually complete conversion of the hexose to D-erythrose. With one mole of oxidant, D-arabinose as well as D-erythrose is obtained (23). The oxidation is carried out in acetic acid solution by the addition of two moles of the powdered oxidant per mole of glucose. Removal of the divalent lead and distillation of the solvent affords a clear, colorless sirup, in 90 to 95% yield, which exhibits the properties of a diformate ester of D-erythrose (24). The ester groups are easily hydrolyzed by heating in water or dilute acid, giving a product which has an equilibrium specific rotation of about $-30°$ and which is uncontaminated by hexose or pentose sugars (paper chromatogram). The infrared absorption spectrum of the free sugar, using the potassium bromide

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window technique (27), is identical with that of D-erythrose prepared from 4,6-*O*-ethylidene-D-glucose (25), and gives no indication of the presence of other compounds. The compound has been further characterized as D-erythrose by hydrogenation to erythritol, by oxidation with bromine to D-erythrono-γ-lactone, and by preparation of the crystalline 2,5-dichlorophenylhydrazone.

On paper chromatograms the new preparation of D-erythrose and the sample prepared from ethylidene glucose behave in identical fashion but show complex properties. For example, each gives a single equally-fast-travelling spot when the solvent is ethyl acetate/acetic acid/water (3/1/3) (15), but in butanol/ethanol/water (4/1/5) (2) much streaking from the origin almost to the solvent front is observed. When an aqueous solution of either preparation is frozen, then thawed, and examined on the chromatogram with the use of methyl ethyl ketone/water (4), at least two spots are found, the major component having an R_f of 0.22 and the other remaining close to the origin. The proportion of slow-moving component is, however, less if the solution is first heated on the boiling-water bath before chromatographing. This behavior may be related to gross changes in optical rotation which have been observed when a solution of the sugar is frozen and thawed. Thus, a solution of D-erythrose having an equilibrium specific rotation of $-31°$, after freezing for 18 hr. and thawing, had a specific rotation of about $-6°$, reverting to the original value during a period of four hours at room temperature. The specific rotation changed to $+2°$ when the solution was stored in the frozen state for 48 hr. These results suggest that D-erythrose in solution readily enters into loose intermolecular association possibly with formation of a dimer or other complex. Such behavior has long been recognized with glyceraldehyde (35), but appears not to have been reported for tetroses. The observed mutarotation changes might therefore correspond to a polymer ↔ monomerfuranose interconversion together with attainment of an α,β-anomer equilibrium for the latter. Perhaps this complexity in part accounts for the wide variation in specific rotations reported for erythrose, such as $-14.5°$ for the D-isomer and $+32.7°$ for the L-isomer (33). Further, the tendency of D-erythrose to associate or dimerize may explain why attempts to crystallize the compound have been unsuccessful.

Pentoses also quickly consume two moles of lead tetraacetate and it was therefore to be expected, by analogy with hexoses, that the degradation should yield the corresponding triose. D-Glyceraldehyde, first prepared by Wohl and Momber (34), is readily obtainable through the elegant method of Fischer and Baer (5), which involves periodate or lead tetraacetate oxidation of 1,2;5,6-di-*O*-isopropylidene-D-mannitol, and, more directly, through the procedure recently reported by Schöpf and Wild (28) in which D-glucose is oxidized with three moles of periodate. By contrast, L-glyceraldehyde is not as easily obtained since the methods just noted require the corresponding but rare L-sugars. Thus Baer and Fischer (2) prepare L-glyceraldehyde from 1,2;5,6-di-*O*-isopropylidene-L-mannitol which is first synthesized from L-arabinose *via* the cyanohydrin reaction and reduction. With lead tetraacetate oxidation, however, L-arabinose is degraded directly to L-glyceraldehyde in high yield. As with D-erythrose the product is recovered from the reaction as

a sirupy formate ester (24), which yields the free glyceraldehyde upon hydrolysis in water or dilute acid. The compound gives an elongated spot on the chromatogram (ethyl acetate/acetic acid/water solvent) with a rate of travel slightly smaller than D-erythrose, possibly due to its existence as a dimer. Traces of arabinose and erythrose were detected in some preparations. The butanol solvent causes much streaking of material on the chromatogram and several spots are discernible, but these are attributed at present to the various modifications possible for glyceraldehyde (2). It will be remembered that erythrose also behaved atypically with this solvent. The equilibrium specific rotation of the compound in water, $[\alpha]_D^{25}$ $-7°$, is close to the value of $+9°$ reported for a freshly-prepared solution of the D-isomer (3). The relatively high purity of the preparation is indicated by the fact that it gave a 73% yield of the L-glyceraldehyde dimedon, which agreed well with the yield of 75% obtained by Baer and Fischer from pure L-glyceraldehyde (2). The product was characterized further as the crystalline 2,4-dinitrophenylhydrazone.

Since oxidation of other aldohexoses and aldopentoses by lead tetraacetate parallels the foregoing oxidations, it is seen, for example, that D-threose may readily be prepared directly from D-galactose and D-glyceraldehyde from D-xylose. A description of their preparation is included in another communication (24), which considers the mechanism of the lead tetraacetate oxidation of reducing sugars.

EXPERIMENTAL

Lead tetraacetate was prepared according to the procedure of Vogel (31). A commercial sample (Matheson Co., Inc.) was also used. All other chemicals were reagent grade.

Spray reagents used for chromatography were triphenyltetrazolium chloride (32), silver nitrate (21), and aniline (22).

Solutions were concentrated *in vacuo* at 35° C.

Di-O-formyl-D-erythrose

D-Glucose (1.50 gm., 8.3 mM.) dissolved in 3 ml. of water was taken up in 150 ml. of glacial acetic acid. Lead tetraacetate[2] (7.7 gm., 17.4 mM.) was added over a period of three to four minutes to the rapidly stirred solution. Within five minutes' reaction time the lead tetraacetate had dissolved and the solution gave a faint potassium iodide – starch test. Oxalic acid dihydrate (1.9 gm.), dissolved in glacial acetic acid, was added,[3] and the suspension was stirred for an additional 30 min. The precipitate was filtered and washed with acetic acid and the filtrate was concentrated to a volume of a few milliliters. Ethyl acetate was added and the precipitate which formed was triturated with several portions of ethyl acetate. The extracts were combined, filtered, and concentrated to a sirup which was further purified twice by extraction with ethyl acetate. The product was a clear, pale yellow oil. Weight, 1.30 gm. This

[2]*If the compound was dark it was recrystallized before use from acetic acid. Or, it was dissolved in glacial acetic acid and the solution was filtered and added to the glucose solution.*

[3]*Excess lead tetraacetate was thereby decomposed and the divalent lead precipitated.*

compound, which is described in greater detail elsewhere (24), is found to contain two formate ester groups.

D-Erythrose

Di-*O*-formyl-D-erythrose (0.201 gm.) was dissolved in 20 ml. of 0.05 *N* hydrochloric acid (a slight turbidity was removed by filtering) and the solution was heated at 50° C., the hydrolysis being followed polarimetrically: $[\alpha]_D$ +0.55° (initial) → −0.40° (two hours, constant). The reducing power of the hydrolyzate, measured by hypoiodite oxidation (8), was equivalent to 0.122 gm. of tetrose (91%); $[\alpha]_D^{27}$ −32.7°. Acid was removed by use of a column (1 cm. × 10 cm.) of Amberlite IR4B resin with some loss of reducing power. The calculated weight of D-erythrose was 0.114 gm., an over-all yield from D-glucose of 80% of theory. $[\alpha]_D^{27}$ −30.0° (equilibrium) (*c*, 0.64).

Erythritol

Di-*O*-formyl-D-erythrose (1.0 gm.) was dissolved in absolute alcohol (40 ml.) and was hydrogenated at ambient temperature and pressure using reduced platinum oxide catalyst (1). Fifty milliliters of hydrogen was taken up, corresponding approximately to one mole per mole of erythrose, and the solution was then only faintly reducing to Fehling's solution. The catalyst was filtered and the filtrate concentrated to a colorless sirup which quickly crystallized. After washing with alcohol and drying the product weighed 0.25 gm. (73%); m.p. 114–116° C. Recrystallization from alcohol raised the melting point to 118° C.; the mixed melting point with an authentic specimen of erythritol (m.p. 118.5° C.) was 118–118.5° C. The X-ray diffraction pattern was identical with that of erythritol.

D-Erythrono-γ-lactone

Barium carbonate (10 gm.) was suspended in an aqueous solution of D-erythrose (2.0 gm. in 30 ml.), and bromine (3.4 ml.) was added dropwise with stirring. After three hours' reaction time excess bromine was removed by aeration, and there were added in succession silver carbonate to remove bromide, hydrogen sulphide gas to remove excess silver, and dilute sulphuric acid to precipitate excess barium. The final colorless solution was concentrated, giving a sirup which solidified when dried in high vacuum at 60° C. Weight, 1.3 gm. (65%). After one recrystallization from alcohol, m.p. 103–104° C., $[\alpha]_D^{27}$ −72.1° (*c*, 1, water); (m.p. 103° C., $[\alpha]_D$ −73.3° (26)).

D-Erythrose 2,5-Dichlorophenylhydrazone

D-Erythrose sirup (0.44 gm.), prepared by concentrating an aliquot of the neutral solution described above, was taken up in 20 ml. of methanol in an evaporating dish. 2,5-Dichlorophenylhydrazine (0.65 gm.) was added and the methanol was rapidly distilled on the steam bath (procedure of Mandl and Neuberg (17)). The product was dissolved in ether, filtered, and the ether was distilled. The residue was dissolved in ethyl acetate, treated with charcoal, and an equal volume of benzene was added. Crystallization was rapid in the cold. Weight, 0.68 gm. (68%), m.p. 101–105° C. Recrystallized twice from

ethyl acetate – benzene (1:1), m.p. 110–112° C., $[\alpha]_D^{27}$ −12.5° (*c*, 1, methanol). (m.p. 110° C. (19)). Calc. for $C_{10}H_{12}O_3N_2Cl_2$: N, 10.04%; found: N, 10.06%.

By using an excess of the hydrazine reagent (1.6 moles per mole) and distilling off three successive additions of methanol containing a few drops of acetic acid, an osazone was obtained. Melting point after recrystallization from ethyl acetate – benzene (1:1), 219–220° C. Calc. for $C_{16}H_{14}O_2N_4Cl_4$: N, 12.81%; found: N, 12.85%.

L-Glyceraldehyde

The method for preparation of the L-glyceraldehyde formate ester was the same as for di-*O*-formyl-D-erythrose differing only in the quantities of oxidant and oxalic acid used. L-Arabinose (1.5 gm.) was oxidized with 9.0 gm. of lead tetraacetate and most of the lead was removed by the addition of 2.5 gm. of oxalic acid dihydrate dissolved in acetic acid. The product obtained by ethyl acetate extraction was a clear, pale yellow oil. Weight, 1.2 gm. This compound, which is described in greater detail elsewhere (24), is found to contain about 1.5 formate ester groups.

The ester (0.201 gm.) was hydrolyzed to constant rotation in 10% acetic acid at 50° C. (7.5 hr.), and the acid was removed by distillation. The quantity of sugar estimated by hypoiodite oxidation was 0.102 gm., corresponding to a yield of L-glyceraldehyde from the ester of 83% $[\alpha]_D^{27}$ −7.15° (equilibrium) (*c*, 2).

Dimedon-L-glyceraldehyde

L-Glyceraldehyde formate ester (1.02 gm.) in 100 ml. of phosphate buffer (containing 10 ml. of 1 *M* monopotassium phosphate and 5.9 ml. of 1 *N* sodium hydroxide) was treated with 2.0 gm. of dimedon at room temperature. After 18 hr. reaction time the solution was concentrated and the crystalline product was recovered by filtration. Weight, 1.73 gm. (73%), m.p. 191–200° C. Two recrystallizations from 50% alcohol raised the melting point to 196.5–198.5° C.; $[\alpha]_D^{27}$ −208° (*c*, 0.5, ethanol), (m.p. 198° C., $[\alpha]_D$ −198° (2)). Calc. for $C_{19}H_{26}O_5$: C, 68.24%; H, 7.84%; found: C, 67.97%; H, 7.86%.

L-Glyceraldehyde-2,4-dinitrophenylhydrazone

To a solution of L-glyceraldehyde (0.71 gm.) in 25 ml. of water, cooled in an ice-bath, was added a slightly warm solution of 2,4-dinitrophenylhydrazine (1.6 gm.) in 2 *N* hydrochloric acid (90 ml.) over a period of 30 min. The reaction mixture was maintained at 0° C. for an additional 30 min. A copious yellow precipitate which formed was filtered, then washed with dilute hydrochloric acid and water, and dried. Weight, 0.97 gm., m.p. 120–140° C. Recrystallized three times from 50% alcohol, m.p. 146–148° (m.p. 147–148° (2)). Calc. for $C_9H_{10}O_6N_4$: C, 40.00%; H, 3.73%; found: C, 40.09%; H, 3.83%.

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MECHANISM FOR THE FORMATION OF GUANIDINE FROM UREA AND AMMONIUM SULPHAMATE[1]

By Jean L. Boivin and A. L. Lovecy

ABSTRACT

The over-all mechanism of the formation of guanidine from urea and ammonium sulphamate is briefly discussed. Experimental results are presented, indicating that primary formation of the ammonium salt of ureasulphonic acid and subsequent dissociation into cyanamide and ammonium sulphate, which further react to form guanidine in the known manner, constitute the main steps in the process.

The essential process of conversion of urea to guanidine may be described as the ammonolysis of urea:

[1] $$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} \rightleftharpoons \begin{matrix} NH \\ \| \\ C{-}OH \\ | \\ NH_2 \end{matrix} + NH_3 \rightleftharpoons \begin{matrix} NH \\ \| \\ C{-}NH_2 \\ | \\ NH_2 \end{matrix} + H_2O\,.$$

Although this equilibrium reaction has been stated to occur in liquid ammonia, there is no reliable evidence that an acceptable yield is obtainable. Blair (2) obtained a 23% yield; Sander (6) using aluminum, aluminum chloride, or phosphorus pentoxide to remove the water formed reported yields of 90%.

In considering possible dehydrating agents to remove the water formed and so assist the completion of the equilibrium reaction (Eq. [1]), sulphur trioxide or its reaction products with ammonia are attractive (5) from the viewpoint of economy and availability:

[2] $$H_2N{-}SO_3NH_4 + H_2O \rightarrow (NH_4)_2SO_4.$$

Combining equation [2] with [1] gives the following over-all equation:

[3] $$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + H_2N{-}SO_3NH_4 \rightarrow \begin{matrix} NH_2 \\ | \\ C{=}NH\,. \\ | \\ NH_3.NH_4SO_4 \end{matrix}$$

Whilst in fact urea does react with sulphamic acid to produce guanidine the reaction is not adequately described by the simple dehydration process indicated above (Eq. [3]), since the following facts must be explained: The fusion of equimolar quantities of urea and sulphamic acid yields traces of guanidine; substitution of ammonium sulphamate gives a pronounced increase in yield mainly when an excess of the former is used (5). Ammonium sulphamate does not in fact react readily with water (3).

In view of these facts, there is no evidence that the reaction-sequence involves an initial dehydration of urea (Eq. [1]) with subsequent or simultaneous interaction of ammonium sulphamate with the water formed (Eq. [2]).

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In seeking an alternative mechanism, it is reasonable to consider the elimination of ammonia rather than water as the primary step, particularly in view of the observation that ammonia is liberated at a temperature of 140° C.

There are two ways in which this might occur when urea and ammonium sulphamate are fused together:

[4] $$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + H_2N{-}SO_3NH_4 \rightarrow \begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2.HO_3S{-}NH_2 \end{matrix} + NH_3,$$

[5] $$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + H_2N{-}SO_3NH_4 \rightarrow \begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NHSO_3NH_4 \end{matrix} + NH_3.$$

As regards equation [4], attempts to prepare a definite urea salt of sulphamic acid were unsuccessful. When an aqueous solution containing equimolar quantities of the base and acid was evaporated to dryness, and the solid obtained was extracted with alcohol, a solution of urea and a residue of sulphamic acid were obtained.

Attention was therefore turned to the second alternative (Eq. [5]), i.e. the formation of ammonium ureasulphonate. Ureasulphonic acid itself has been prepared by the sulphonation of urea with sulphur trioxide and is an intermediate in the formation of sulphamic acid as described by Baumgarten (1). It has now been prepared in 60% yield by treatment of urea with sulphuric acid and acetic anhydride at low temperature, whereby a viscous product separates, believed to be the urea salt of ureasulphonic acid. By dissolving this material in absolute ethanol and passing in gaseous ammonia a crystalline compound was obtained, m.p. 168–170° C.; this was the ammonium salt of ureasulphonic acid, described by Linhard (4).

By fusion of this salt alone at 240° C. a yield of guanidine equivalent to 43–45% of the theoretical was obtained (estimated as the picrate). Melamine was also shown to be present in 22% yield. This result indicates that ureasulphonic acid may be involved in the conversion of urea to guanidine. Heating under a pressure of ammonia was tried, the ammonia being introduced as liquid. At a pressure of 1500 p.s.i. and 295° C., the yield of guanidine obtained after one and one-quarter hours was 63%, and at a pressure of 200 p.s.i. and 300° C., the yield of guanidine was only 10% but melamine was formed in 77% yield.

A reaction based on the formation of cyanic acid from urea would also explain the mechanism:

[6] $$NH_2{-}CO{-}NH_2 \rightleftharpoons NH_4OCN \rightleftharpoons NH_3 + HOCN,$$

[7] $$HOCN + NH_2SO_3NH_4 \rightarrow NH_4SO_3{-}NH{-}CO{-}NH_2.$$

The formation of cyanic acid takes place at temperatures upwards of 140° C. and it seems that this active fragment reacts with sulphamic acid to form ureasulphonic acid. Actually, a 57% yield of the latter compound has been

isolated from a melt of urea with ammonium sulphamate, carried out at a temperature not exceeding 140° C. under reduced pressure.

Assuming the primary formation of ammonium ureasulphonate as probable, its subsequent conversion to guanidine is still by no means obvious. It is conceivable that a further dissociation and rearrangement is involved, particularly since a temperature in the region of 290° C. seems necessary in order to obtain a good yield.

By analogy with the fusion of amides with ammonium sulphamate or the intermediate product, ammonium N-alkylsulphamates, which are transformed into high yields of nitriles (3), it seems that ammonium ureasulphonate should produce the corresponding nitrile which is cyanamide (Eq. [8]).

[8] $$\begin{array}{l} NH_2 \\ | \\ C{=}O \\ | \\ NHSO_3NH_4 \end{array} \rightarrow \begin{array}{l} NH_2 \\ | \\ C{\equiv}N \end{array} + NH_4HSO_4$$

[9] $$\begin{array}{l} NH_2 \\ | \\ C{\equiv}N \end{array} + (NH_4)_2SO_4 \rightarrow \begin{array}{l} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2.NH_4SO_4 \end{array}$$

It is well known that cyanamide in the presence of ammonium salt is quickly transformed into guanidine (Eq. [9]) or its trimer, melamine.

EXPERIMENTAL

Ammonium Ureasulphonate

To a cold solution (−20° C.) of acetic anhydride (250 ml.) and sulphuric acid (95%, 48 gm., 0.5 mole) was added a solid feed of finely powdered urea (60 gm., 1.0 mole). The temperature of the mixture was allowed to rise slowly to 15° C. with occasional stirring. Urea dissolved completely, and at 15–18° C. a viscous product was formed which was decanted. This oily material was dissolved in absolute ethanol (500 ml.) (methanol is not suitable). The solution was chilled to −30° C. and saturated with gaseous ammonia. A crystalline compound separated out. It was filtered, washed thoroughly with ether, and dried, m.p. 167.5–168° C. with decomposition. Yield, 47 gm. (60% from sulphuric acid). The urea in excess may be recovered by evaporation of the filtrate.

This ammonium ureasulphonate was hydrolyzed quantitatively with dilute nitric acid to urea nitrate and sulphuric acid. By treatment of this substance with concentrated sulphuric acid, sulphamic acid is obtained (1).

Guanidine from Ammonium Ureasulphonate

(*A*) This ammonium salt (5.1 gm.) was heated at 225–230° C. for one-half hour. The residue was dissolved in water and analyzed for guanidine and melamine. Guanidine: 0.8 gm. (42%); melamine: 22%.

(*B*) The same ammonium salt (5.3 gm., 0.03 mole) and liquid ammonia (20 ml.) were heated in a closed vessel at 295° C. for 75 min. at a pressure of 5100 p.s.i.g. Guanidine: 63%; melamine was absent.

(*C*) The same reaction was effected as above, but conditions were the following: temp.: 300° C.; heating time: 17 hr.; pressure: 200 p.s.i.; melamine: 77%; guanidine: 10%.

Preparation of Ammonium Ureasulphonate from Urea and Ammonium Sulphamate

Urea (6.0 gm., 0.1 mole) and ammonium sulphamate (11.7 gm., 0.1 mole) were heated at 135–140° C. under reduced pressure (15 mm.) in order to eliminate the ammonia formed in the reaction. The heating was effected during six hours. The reaction mixture was boiled with 85% ethanol. On cooling, a crystalline compound separated out. It was filtered and dried, m.p. 165–166° C. By working up the filtrate, it was possible to isolate 9.1 gm. of this material (57%). A portion of this solid was recrystallized from ethanol. It melted at 167–168° C. A mixed melting point with an authentic sample was not depressed.

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INFRARED AND RAMAN SPECTRA OF 1-CHLOROPROPYNE AND 1-CHLOROPROPYNE-d_3[1]

By D. W. Davidson[2] and H. J. Bernstein

ABSTRACT

The infrared spectra of 1-chloropropyne and 1-chloropropyne-d_3 have been investigated in the vapor state, in solution, and, in part, in the liquid over the spectral region 3 to 35μ. Intensities of the infrared bands have been measured from the spectra of the solutions. The Raman spectra of the compounds in the liquid state, together with standard intensities and depolarization ratios of the Raman bands, were obtained. A complete assignment, based on a normal coordinate calculation of the fundamentals, has been made. Coriolis coupling coefficients of three of the perpendicular-type fundamentals of $CH_3C{\equiv}CCl$ were determined and those of the other two shown to be near unity. Two coupling coefficients for $CD_3C{\equiv}CCl$ were obtained. The potential function and isotope effects on Raman intensity and Raman displacement of the CCl stretching vibration are discussed.

INTRODUCTION

1-Chloropropyne (methylchloroacetylene: $CH_3C{\equiv}CCl$) has been investigated previously by Cleveland and Murray (5), who obtained the Raman spectrum of the liquid, as prepared by a Grignard reaction from methylacetylene. These Raman bands were tentatively assigned by Meister (14), with the aid of a normal coordinate treatment. Parts of the chloropropyne spectrum were obscured, however, by lines arising from the presence of ethyl bromide in considerable quantity in the sample. Morse and Leitch (15) have recently reported a more efficient synthesis and have provided us with a sample both of $CH_3C{\equiv}CCl$ and of the completely deuterated form $CD_3C{\equiv}CCl$ (1-chloropropyne-d_3). We have investigated the vibrational spectra of these molecules and confirm Meister's assignment of fundamentals for $CH_3C{\equiv}CCl$.

Methylchloroacetylene belongs to the C_{3v} symmetry point group and possesses five normal vibrations of symmetry type A_1 and five doubly degenerate E-type vibrations. With the exception of $\nu_{10}(e)$, all the fundamentals in both molecules have been observed. Assignments have been made for the combination bands, although in some cases it has not been possible to choose between alternative assignments. Sum and difference bands involving $\nu_{10}(e)$ have been used to fix approximately the frequency of this mode.

An attempt has been made to measure the intensities of prominent bands in both the infrared and Raman spectra and the depolarization ratios of the stronger Raman bands. The Coriolis coupling coefficients were determined for the fundamental bands of the perpendicular type, wherever these were resolved.

EXPERIMENTAL METHODS

The infrared data were obtained with a single beam double pass Perkin-Elmer spectrometer (Model 112) using LiF, CaF_2, NaCl, KBr, and CsBr

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prisms. Window materials were KBr, except for the CsBr region where windows of KI-TlI were used. Except for a few strong bands, which were examined also at lower pressures, vapor spectra were obtained at the vapor pressure of the liquid at 22°C. For $CH_3C{\equiv}CCl$ and $CD_3C{\equiv}CCl$ these pressures were approximately 530 and 560 mm., respectively.[3] Band intensities were determined for spectra obtained in solutions in CS_2 or CCl_4. The solution spectra were useful also for resolving bands which overlap in the vapor spectra, and, together with the liquid spectra recorded at low frequencies, for detecting weak bands.

Raman spectra of $CH_3C{\equiv}CCl$ were recorded by two methods. In the first, as in previous work (2), a double-prism photographic instrument ($f/3.5$, dispersion 29 Å/mm. at 5000 Å) was used. The second instrument was a new photoelectric-recording grating spectrometer (21), constructed by the White Development Corporation, Stamford, Connecticut. The photoelectric instrument has the advantage of speed and simplicity in the determination of relative intensities and depolarization ratios. The method of Edsall and Wilson (8) was used to measure depolarization ratios. The Raman spectrum of $CD_3C{\equiv}CCl$ was obtained with the photoelectric instrument only. Both liquids turned yellowish under mercury radiation, although the effect was considerably reduced when a filter consisting of a saturated aqueous solution of $NaNO_2$ was placed between the mercury source and the Raman tube. This filter also practically eliminated excitation by the Hg > 4047 line.

RESULTS

The infrared spectra are shown in Figs. 1 and 2 and the observed bands listed in Tables I and II. The photoelectrically-recorded Raman spectra are reproduced in Fig. 3 and the data given in Tables III and IV.

Most of the observed infrared and Raman bands could be satisfactorily ascribed to $CH_3C{\equiv}CCl$ or $CD_3C{\equiv}CCl$. Near 800 cm.$^{-1}$, however, absorption occurred in solution spectra of both molecules, although it was absent in the vapor spectra. It was greatly reduced by distillation and is attributed to traces of grease.

The results of Cleveland and Murray (5) are included in Table III. The band observed by them at 184 cm.$^{-1}$ was not observed directly in the present work, probably because of its weakness and interference from grating ghosts in this part of the spectrum. Nor was the corresponding band in the spectrum of $CD_3C{\equiv}CCl$ observed.

INTENSITIES OF INFRARED BANDS

Integrated extinction coefficients (ϵ) for the solution bands (Tables I and II) were calculated from the maximum optical density ($d_{max.} = \log_{10} I_0/I$) and the band width ($\Delta\nu_{\frac{1}{2}}$) at half-maximum intensity, assuming the Lorentz band shape. The small correction for finite spectral slit width (s) was incorporated in ϵ by multiplying $d_{max.} \cdot \Delta\nu_{\frac{1}{2}}/c.l$ by the factor K, usually not quite $\pi/2$, as tabulated by Ramsay (16). The concentration c has been expressed in moles

[3] *These values were derived by an extrapolation of the vapor pressure vs. temperature curves of Morse and Leitch (15).*

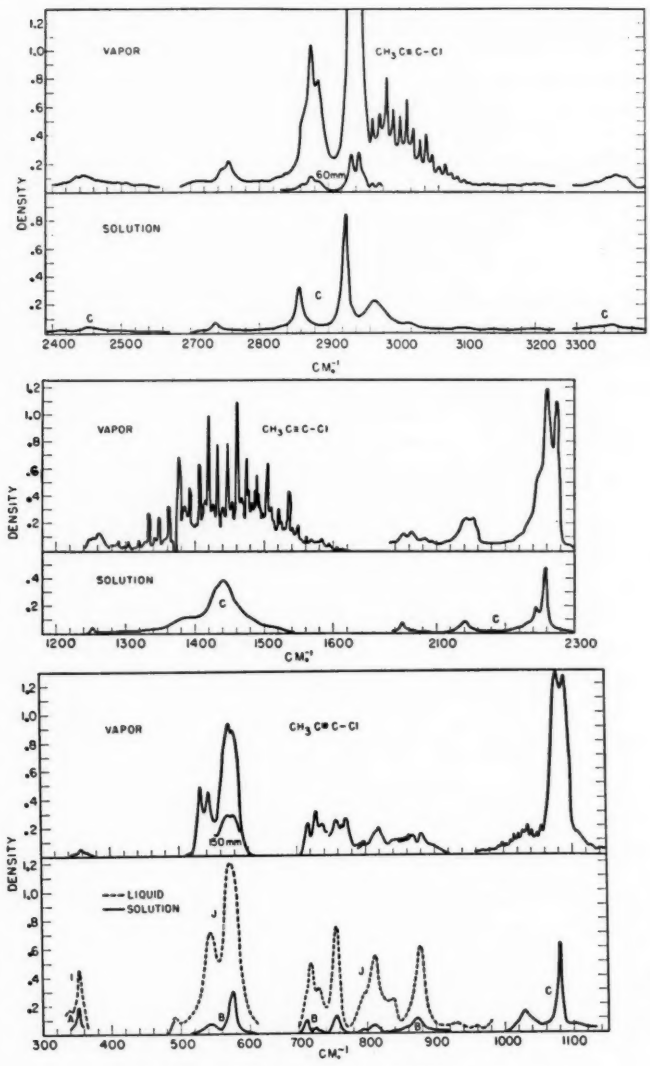


FIG. 1. Infrared spectra of $CH_3C{\equiv}C{-}Cl$.

per liter and the cell thickness l in centimeters. The value of s was taken to be half the spectral slit width for single pass optics.

DEPOLARIZATION RATIOS AND INTENSITIES OF RAMAN BANDS

Because of the convergence of light from the source on the Raman tube, the observed depolarization ratio ρ has been corrected to give the true value

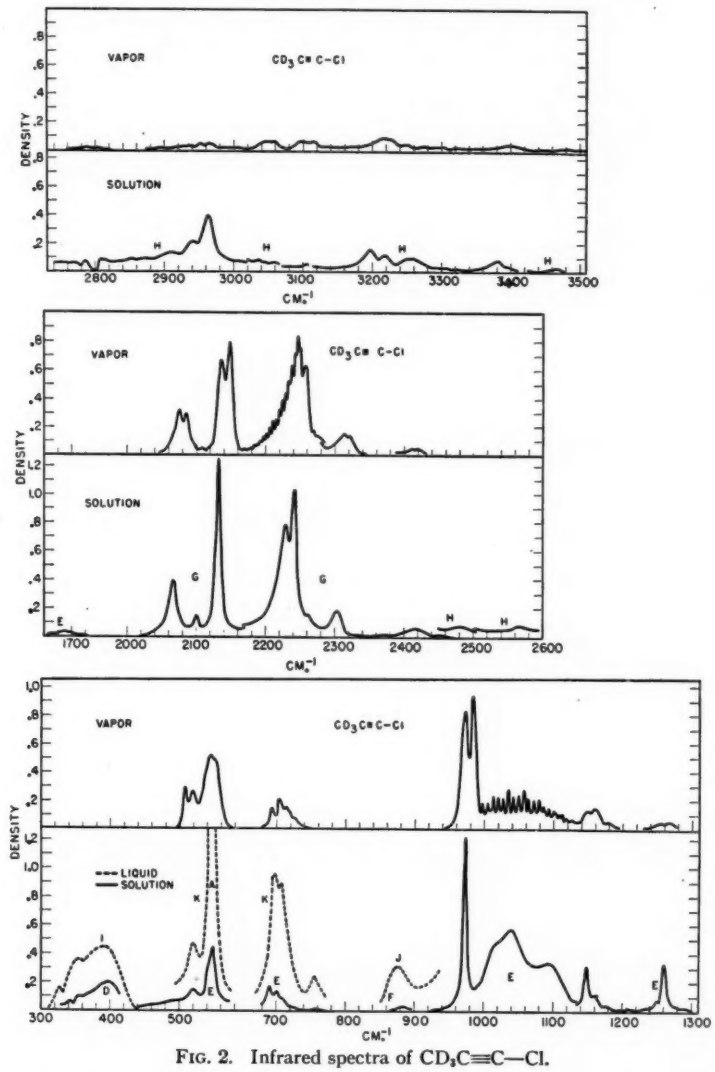


FIG. 2. Infrared spectra of $CD_3C{\equiv}C{-}Cl$.

ρ_t essentially according to the method of Rank and Kagarise (17). Values of ρ and ρ_t are given in Tables III and IV.

These tables include also the peak intensity (i) relative to that of the $\nu_1(a_1)$ band (taken as $i = 100$) which includes the correction for the spectral sensitivity of the IP21 photomultiplier. The observed half-band widths ($\Delta\nu_{\frac{1}{2}}$) and spectral slit width s are also given and the standard intensity S referred to the 458 cm.$^{-1}$ band in CCl_4 for each band obtained from the equation (1).

[1] $$S = \frac{I}{I_{458}} \frac{1+\rho_{458}}{1+\rho} \frac{n^2}{n^2_{CCl_4}} \frac{\sigma_{\Delta\nu}}{\sigma_{458}} \frac{R(n)}{R_{CCl_4}} \frac{M}{d} \left(\frac{d}{M}\right)_{CCl_4} \times \frac{\Delta\nu}{458} \left(\frac{\nu-458}{\nu-\Delta\nu}\right)^4 \frac{1-e^{-1.44\Delta\nu/T}}{1-e^{-1.44\times458/T}}.$$

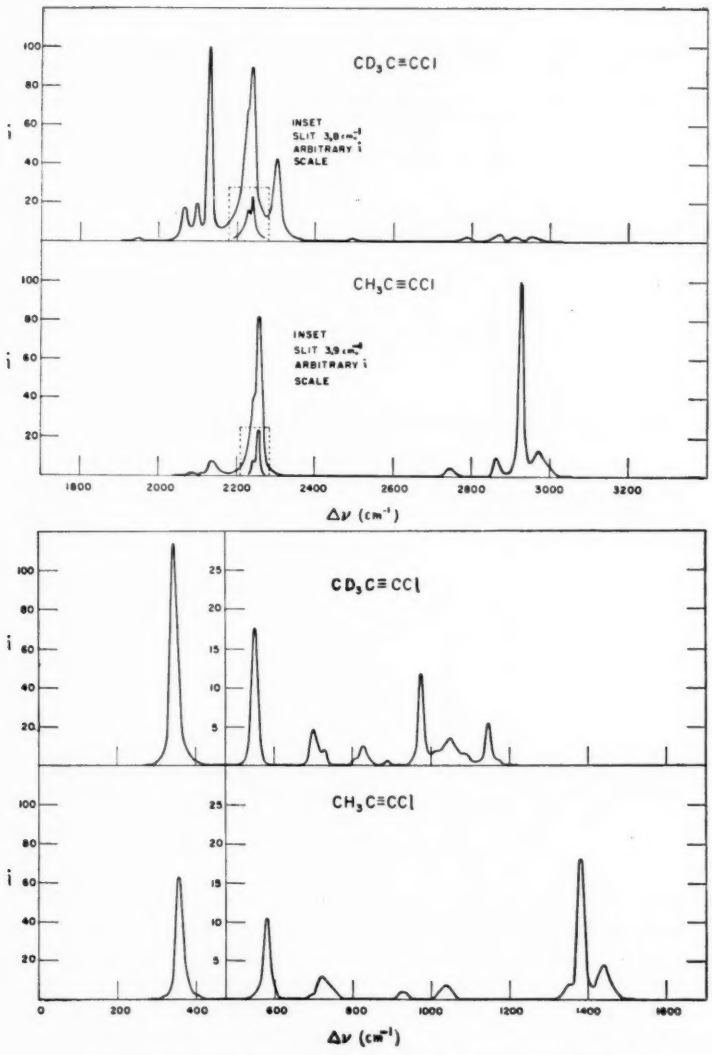


FIG. 3. Raman spectra of liquid $CH_3C{\equiv}C{-}Cl$ and $CD_3C{\equiv}C{-}Cl$.

TABLE I

INFRARED DATA FOR $CH_3C{\equiv}CCl$

Vapor			Solution						Liquid		
$\nu_{vac.}$, cm.$^{-1}$	s, cm.$^{-1}$	Band character	$\nu_{vac.}$, cm.$^{-1}$	Conditions	$d_{max.}$	$\Delta\nu_{\frac{1}{2}}$, cm.$^{-1}$	s, cm.$^{-1}$	ϵ^*	$\nu_{vac.}$, cm.$^{-1}$	Conditions	Assignments
358	2.1		351.8	A	0.193	8.5	4.2	35	353.2	I	$\nu_9(e)$
536.8	2.1	Doublet	544	A_1	0.58	28	1.9	157	544	J	$\nu_9(e)+\nu_{10}(e) = 542$
575.3	2.1	Doublet	576	B	0.32	12	2.6	180	573	J	$\nu_5(a_1)$
721	2.5	Doublet	713	B	0.090	~10	4.1	~ 40	718	J	$\{2\nu_9(e)=716; \nu_9(e)+2\nu_{10}(e)=726\}$
734.2	2.6	Doublet	725	B	0.030	~ 9	2.7	~ 13	729	J	$\{\nu_4(a_1)-\nu_9(e)=726\}$
765	2.5	Triplet	755.6	B	0.116	10	3.1	55	754.8	J	$\nu_5(a_1)+\nu_{10}(e) = 759$
819	3.1	Single pk.?	811	B	0.054	13	2.6	30	810	J	$\nu_3(a_1)-\nu_5(a_1) = 820$
840	3.1								836	J	$\nu_8(e)-\nu_{10}(e) = 849$
874.8	2.4	Doublet	871.5	B	0.097	14	3.3	65	876	J	$\nu_7(e)-\nu_5(a_1) = 878$
1033.0	3.1	K-structure	1029.3	C	0.155	21	3.7	157	1025.5	J	$\nu_8(e)$
1083.6	3.8	Doublet	1080.3	C	0.63	8.7	4.5	250	1074.5	J	$\nu_4(a_1)$
1257.5	3.4	Doublet	1252.2	C	0.046		4.2	w			$\nu_7(e)-\nu_{10}(e) = 1270$
~1395	3.8	Doublet	~1379	C	~0.041		5.8	w			$\nu_3(a_1)$
1453.7$_8$	2.7	K-structure	1440.0	C	0.385	~48	6.7	~890			$\nu_7(e)$
2058.5	1.6	Doublet	2050.5	C	0.075	8.5	2.8	30			$2\nu_8(e) = 2066$
2089	1.8	Doublet	2079	C	0.060		1.2				$\nu_3(a_1)-\nu_{10}(e) = 2084$
2149	2.0	Doublet	2141	C	0.085	17	3.2	69			$2\nu_4(a_1) = 2168$
~2222	2.0	Single pk.?	2219	C	~0.030		3.5				$\{\nu_3(a_1)+n\nu_1(e)$
~2233	2.0	Single pk.?	2231	C	~0.030		3.5				$\{-n\nu_1(e)\}$
2252	2.0	Doublet	2245	C	0.14	~15	3.6	~100			
2267.7	2.0	Doublet	2258	C	0.48	7.6	3.7	165			$\nu_2(a_1)$
2444.5	2.2		2451	C	~0.030		3.4				$\nu_3(a_1)+\nu_{10}(e) = 2452$
2749	3.0	Doublet	2736	C	0.065	~19	4.7	~ 58			$\nu_1(a_1)-\nu_{10}(e)=2755;$ $2\nu_2(a_1) = 2790$
2875.5	3.5	Triplet?	2857.5	C	0.320	14	5.4	207			$2\nu_7(e) = 2906$
2939.2	3.7	Doublet	2924.8	C	0.837	10.3	5.8	396			$\nu_1(a_1)$
2980.0	2.9	K-structure	2967.3	C	0.225	43	6.1	466			$\nu_6(e)$
~3198	3.5	Broad pk.									$\nu_6(e)+\nu_{10}(e)=3164;$ $\nu_1(a_1)+\nu_9(e) = 3297$
~3357	4.1	Broad pk.	~3351	C	~0.030	~21	6.1	~ 30			$\nu_2(a_1)+\nu_4(a_1) = 3352$

Letters under "Conditions" identify the solvent, concentration, and cell in the case of solutions and the cell in the case of liquids:

A 2.7 M./l. in CS_2, 0.25 mm. KI-TlI cell,
A_1 same solution in 0.60 mm. KBr cell,
B 1.35 M./l. in CS_2, 0.24 mm. KBr cell,
C 1.35 M./l. in CCl_4, 0.24 mm. KBr cell,
I liquid in 0.25 KI-TlI cell,
J in 0.24 mm. KBr cell,
**ϵ is the integrated extinction coefficient in mole^{-1} liters cm^{-2}.*

TABLE II

INFRARED DATA FOR $CD_3C{\equiv}CCl$

Vapor			Solution						Liquid		
$\nu_{vac.}$, cm.$^{-1}$	s, cm.$^{-1}$	Band character	$\nu_{vac.}$, cm.$^{-1}$	Conditions	$d_{max.}$	$\Delta\nu_{\frac{1}{2}}$ cm.$^{-1}$	s, cm.$^{-1}$	ϵ	$\nu_{vac.}$, cm.$^{-1}$	Conditions	Assignments*
			$\sim$ 341	D	$\sim$0.050	>20	1.9	> 8	327	I	$\nu_3(a_1)-\nu_8(e)$ = 326
			$\sim$ 355	D	$\sim$0.10	Broad	2.3	$\sim$ 15	352	I	$2\nu_{10}(e)$ = 354
			$\sim$ 396	D	$\sim$0.20	>35	2.7	$\sim$ 54	388	I	$\nu_9(e)$
512.8	1.25	Doublet	519.6	E	0.110	20	2.1	70	519.8	K	$\nu_9(e)+\nu_{10}(e)$ = 520
546.8	1.50	Doublet	548.2	E	0.146	14.5	2.4	207	547.3	K	$\nu_5(a_1)$
698.6	1.55	Doublet	689.4	E	0.173	$\sim$10	2.0	$\sim$ 55	696	K	$2\nu_9(e)$ = 686
$\sim$ 714	1.6		701.5	E	$\sim$0.09	$\sim$24	2.1	$\sim$ 69	706	K	$\nu_7(e)-\nu_9(e)$ = 704
? 726	2.1		728	E	$\sim$0.015		2.3				$\nu_5(a_1)+\nu_{10}(e)$ = 724
888	1.6		882	F	0.030		4.1		875	J	$\nu_5(a_1)+\nu_9(e)$ = 890
977.2	1.4	Doublet	972.7	E	1.22	5.5	2.1	214			$\nu_4(a_1)$
			$\sim$1013	E		Broad	2.4				$3\nu_9(e)$ = 1029; $\nu_8(e)+\nu_{10}(e)$ = 1002
1050.8	1.7	K-structure	1038	E	$\sim$0.57	$\sim$27	2.6	$\sim$492			$\nu_7(e)$
$\sim$1107	2.2	Doublet	1095	E	$\sim$0.27	$\sim$35	2.8	$\sim$303			$2\nu_5(a_1)$ = 1094; $\nu_2(a_1)-\nu_3(a_1)$ = 1101
1151	2.4	Doublet	1148	E	0.360	9.0	2.0	103			$\nu_3(a_1)$
$\sim$1159	2.4	Shoulder	1162	E	$\sim$0.060		2.0				$\nu_8(e)+\nu_9(e)$ = 1168; $\nu_4(a_1)+\nu_{10}(e)$ = 1154
?1178	2.1	Single pk.	?$\sim$1177	E	$\sim$0.030		2.1				$\nu_6(e)-\nu_7(e)$ = 1184
$\sim$1260	5.7	Doublet	1260	E	0.34	9.6	1.6	105			$\nu_3(a_1)-\nu_4(a_1)$ = 1275; $\nu_6(e)-\nu_4(a_1)$ = 1258
2080.4	1.7	Doublet	2061	H	0.86	17	3.2	161			$2\nu_7(e)$ = 2102; $\nu_2(a_1)-\nu_{10}(e)$ = 2075
$\sim$2113	1.8	Doublet	2100	G	0.146	10	3.5	45			$\nu_3(a_1)+\nu_4(a_1)$ = 2128
2142.4	1.9	Doublet	2134.8	G	1.26	8.6	3.7	345			$\nu_1(a_1)$
2235.4	2.1	K-structure	2229.3	G	$\sim$0.60	$\sim$28	3.3	$\sim$538			$\nu_6(e)$
2252	2.1	Doublet	2242	G	$\sim$0.60	$\sim$ 6	3.3	$\sim$107			$\nu_2(a_1)$

2273	2.2	Doublet	2262	*G*	~0.05		3.4		$\nu_2(a_1)+\nu_{10}(e)-\nu_{10}(e)$?
2318	2.3	Doublet?	2303	*G*	0.180	20	3.6	115	$2\nu_3(a_1)=2302$; $\nu_1(a_1)+\nu_{10}(e)=2319$
2414	1.9	Doublet?	2416	*H*	0.170	~14	3.1	~ 26	$\nu_6(e)+\nu_{10}(e)=2412$; $\nu_2(a_1)+\nu_{10}(e)=2429$
			~2480	*H*	~0.030		3.2		$\nu_1(a_1)+\nu_9(e)=2485$
			~2566	*H*	~0.030		3.0		$\nu_6(e)+\nu_9(e)=2578$; $\nu_2(a_1)+\nu_9(e)=2595$
~2795	2.9	Doublet	2785	*H*	~0.080		3.8		$\nu_2(a_1)+\nu_5(a_1)=2799$
			~2907	*H*	~0.060		4.3		$\nu_8(e)+2\nu_9(e)=2921$
? 2952	2.5	May together	~2939	*H*	0.13		4.4		$\nu_2(a_1)+2\nu_9(e)=2938$
? 2966	2.5	form a doublet	2963	*H*	0.39	22	4.6	94	$\nu_1(a_1)+\nu_8(e)=2967$
3057		Doublet	3042	*H*	w		3.4		$\nu_6(e)+\nu_8(e)=3060$; $\nu_2(a_1)+\nu_8(e)=3077$
3105		Doublet	3106	*H*	0.056		3.6		$\nu_1(a_1)+\nu_4(a_1)=3119$
3213	3.1	Broad pk.	3197	*H*	0.160	~24	4.0	42	$\nu_4(a_1)+\nu_6(e)=3212$
			3219	*H*	~0.09		4.0		$\nu_4(a_1)+\nu_2(a_1)=3229$
3248	3.3		3255	*H*	~0.10	Broad	4.4		$\nu_6(e)+\nu_7(e)=3286$; $\nu_1(a_1)+\nu_3(a_1)=3293$; $\nu_2(a_1)+\nu_7(e)=3302$
3396	9.3		3380	*H*	0.080	~18	4.7	~ 16	$\nu_2(a_1)+\nu_3(a_1)=3403$
			~3466	*H*	~0.034		5.1		$\nu_1(a_1)+\nu_4(a_1)+\nu_9(e)=3462$

D 2.03 M./l. in CCl_4, 1 mm. cell,
E 2.03 M./l. in CS_2, 0.24 mm. cell,
F 4.06 M./l. in CCl_4, 0.24 mm. cell,
G 2.03 M./l. in CCl_4, 0.24 mm. cell,
H 2.03 M./l. in CS_2, 0.70 mm. cell,
I liquid in 0.25 mm. KI-TlI cell,
J 0.24 mm. KBr cell,
K 0.12 mm. KBr cell,

**Raman values of $\nu_9(e)=343$ cm.$^{-1}$ and $\nu_8(e)=825$ cm.$^{-1}$ are used in evaluating combination bands.*

TABLE III

RAMAN SPECTRUM OF $CH_3C{\equiv}CCl$

Photoelectric instrument							Photographic instrument	Assignments[a]	Observed by Cleveland and Murray
$\Delta\nu_{vac.}$, cm.$^{-1}$	i	$\Delta\nu_{\frac{1}{2}}$, cm.$^{-1}$	s, cm.$^{-1}$	ρ	ρ_t	S	$\Delta\nu_{vac.}$, cm.$^{-1}$		$\Delta\nu_{vac.}$, cm.$^{-1}$
								$\nu_{10}(e) = 184$	184
355	63	19	10.9	0.93	0.78	0.22	±352	$\nu_9(e) = 354$	±353
								$\nu_8(e) - \nu_5(a_1) = 452$	439
579	11	19	10.7	0.32	0.19	0.12	577	$\nu_5(a_1) = 578$	
718	3	~28	10.6	(0.5)[c]		~0.06	725	$2\nu_9(e) = 708$	
								$\nu_8(e) - \nu_{10}(e) = 846$	842[b]
~ 926	~ 0.8	~32	10.3	(0.9)[c]		~0.03		$\nu_5(a_1) + \nu_9(e) = 932$	
~1037	~ 2		10.2				1030	$\nu_8(e) = 1030$	1029
1378	18	20.5	9.8	0.72	0.58	0.47	1380	$\nu_3(a_1) = 1379$	1380
1437	3.6	~28	9.8	~1.0	~0.85	~0.13	1444	$\nu_7(e) = 1443$	1449
~2090	~ 1	~15	9.3			~0.03		$\nu_4(a_1) + \nu_8(e) = 2114$	2102[b]
2138	8.3	20	9.2	0.38	0.24	0.48	2137	$2\nu_4(a_1) = 2168$	2134[b]
2244	~15	~20	3.9	~1.0	~0.85	~0.66	2243	$\nu_2(a_1) + \nu_{10}(e) - \nu_{10}(e)$	2235
2257	69	18	3.9	0.44	0.30	3.99	2259	$\nu_2(a_1) = 2259$	2263
2450	~ 5						2448	$\nu_2(a_1) + \nu_{10}(e) = 2443$	
2740	4	25	8.7	(0.5)[c]		0.38	2734	$2\nu_3(a_1) = 2758$	2733
2862	10	19.5	8.6	0.50	0.36	0.82	2859	$2\nu_7(e) = 2886$	2864[b]
2926	100	14.4	8.5	0.23	0.10	7.00	2926	$\nu_1(a_1) = 2926$	2926[b]
2971	8	~32	8.5	0.93	0.78	1.80	2968	$\nu_6(e) = 2970$	2971[b]
~3117	~ 6		8.3				~3115	$\nu_1(a_1) + \nu_{10}(e) = 3110$	

[a] *Fundamental frequencies given are those regarded as "best" from the Raman data. Wherever possible, the numbers given for the combination bands are evaluated from the "best" values of Raman fundamentals.* $\nu_4(a_1)$ *is taken to be 1084 cm*$^{-1}$.

[b] *These bands observed by Cleveland and Murray correspond approximately to ethyl bromide bands and may be affected by their presence.*

[c] *Parenthesized* ρ*'s are assumed values for the purpose of estimating S.*

TABLE IV

RAMAN SPECTRUM OF $CD_3C{\equiv}CCl$

$\Delta\nu_{vac.}$, cm.$^{-1}$	i	$\Delta\nu_{\frac{1}{2}}$, cm.$^{-1}$	s, cm.$^{-1}$	ρ	ρ_t	S	Assignments[a]
343	132	22.4	10.9	0.90	0.76	0.66	$\nu_9(e)$
551	19.9	18.7	10.7	0.32	0.19	0.22	$\nu_5(a_1)$
701	4.4	∼29	10.6	(0.5)[b]		∼0.09	$2\nu_9(e) = 686$; $\nu_7(e)-\nu_9(e) = 705$
∼ 731	1.4						$\nu_5(a_1)+\nu_{10}(e) = 728$
825	2.9	23	10.4	∼1	∼0.85	0.05_3	$\nu_8(e)$
890	1.0			∼0.6	∼0.4_8		$\nu_5(a_1)+\nu_9(e) = 894$
974	11.7	16.8	10.3	0.77	0.63	0.17	$\nu_4(a_1)$
∼1012	v.w.						$\nu_8(e)+\nu_{10}(e) = 1002$; $3\nu_9(e) = 1029$
1048	2.6	Broad					$\nu_7(e)$
1090	∼ 1						$2\nu_5(a_1) = 1102$; $\nu_2(a_1)-\nu_3(a_1) = 1094$
1146	5.5	18.1	10.1	0.87	0.73	0.11	$\nu_3(a_1)$
1947	1.4						$2\nu_4(a_1) = 1948$
2068	25	21.3	9.3	0.31	0.18	1.80	$2\nu_7(e) = 2096$
2100	22	16.2	9.3	0.36	0.22	1.14	$\nu_3(a_1)+\nu_4(a_1) = 2120$
2131	100	13.5	9.2	0.30	0.17	4.31	$\nu_1(a_1)$
2229	33	∼25.8	3.8	∼1.0	∼0.85	∼2.2	$\nu_6(e)$
2240	57	15.2	3.8	0.4 to 0.5	0.26 to 0.36	∼3.2	$\nu_2(a_1)$
2302	43	22.6	9.0	0.45	0.31	3.50	$2\nu_2(a_1) = 2292$
∼2490	2		8.9				$\nu_1(a_1)+\nu_9(e) = 2474$
2786	2.8		12.9				$\nu_1(a_1)+\nu_6(e) = 2780$; $\nu_1(a_1)+\nu_2(a_1) = 2791$
2868	3.8		12.7				$\nu_1(a_1)+\nu_5(a_1)+\nu_{10}(e) = 2859$
∼2909	2.7	∼23	12.7	(0.5)[b]		∼0.26	$\nu_6(e)+2\nu_9(e) = 2915$; $\nu_2(a_1)+2\nu_9(e) = 2926$
∼2949	2.8	∼22	12.7	(0.9)[b]		∼0.22	$\nu_1(a_1)+\nu_8(e) = 2956$; $\nu_5(a_1)+\nu_6(e)+\nu_{10}(e) = 2957$

[a] *See footnote a, Table III.* $\nu_{10}(e)$ *is taken to be 177 cm*$^{-1}$.
[b] *See footnote c, Table III.*

Here I is the integrated intensity of the band in question,
ρ is the observed depolarization ratio,
n is the refractive index of the material,
$\sigma_{\Delta\nu}$ is the spectral sensitivity of the IP21 tube at the wavelength corresponding to $\Delta\nu$,
$R(n)$ is the reflection loss,
M is the molecular weight and d the density of the material,
$\Delta\nu$ is the wave number of the Raman band,
ν is the wave number of the exciting radiation,
and T is the absolute temperature.

The subscript CCl_4 indicates the corresponding quantities for the reference substance CCl_4, and the subscript 458 refers to the band at 458 cm.$^{-1}$ in CCl_4. In Reference (1) it has been shown that

$$S = \frac{[45(\partial\alpha/\partial Q)^2+7(\partial\gamma/\partial Q)^2]_{\Delta\nu}}{[45(\partial\alpha/\partial Q)^2+7(\partial\gamma/\partial Q)^2]_{458}}$$

where α and γ are the average polarizability and anisotropy respectively and Q is the normal coordinate for the band whose Raman shift is $\Delta\nu$. In obtaining a standard intensity from this formula the integrated intensity has been obtained by using the product of the peak intensity and the observed half-band width and then correcting for the effect of the finite slit width by means of the curves calculated by Bernstein and Allen (1) to give the true integrated intensity. In the above equation the observed intensity has been corrected also for convergence of the incident beam, spectral sensitivity of the detector, the amount of light the spectrometer sees, the amount of light incident on the sample tube; and then expressed as scattering intensity per molecule. The intensities determined in this way are probably accurate to $\pm 10\%$ for the strong isolated bands at 343 cm.$^{-1}$ and 551 cm.$^{-1}$ in $CD_3C{\equiv}CCl$ and at 355 cm.$^{-1}$ and 579 cm.$^{-1}$ in $CH_3C{\equiv}CCl$. Because of overlapping in the region 2000–2400 cm.$^{-1}$ the standard intensities are considerably less accurate.

For $CH_3C{\equiv}CCl$ and $CD_3C{\equiv}CCl$ values of n are given by Morse and Leitch (15). A rough determination of the density gave 1.008 for $CH_3C{\equiv}CCl$ at 25°C. The molecular volume of $CD_3C{\equiv}CCl$ was assumed to be the same as that for $CH_3C{\equiv}CCl$.

CALCULATION OF THE FREQUENCIES

Meister (14) has calculated the fundamental frequencies of methylacetylene-type molecules, $CH_3C{\equiv}C{-}X$, from a potential energy function which includes all eight bond-stretching and -bending force constants and five interaction constants. In our treatment, we have adopted the same potential function and the same symbols for the force constants and the molecular dimensions.

Some of the E elements in the G matrix used by Meister are in error.[4] For the symmetry coordinate R_{1a}, R_{1b}, R_{2a}, . . . R_{5b} chosen by Meister, the values of G_{14}, G_{24}, G_{25}, and G_{34} are to be multiplied by -2. The changes in

[4]*These corrections were pointed out by A. V. Golton in correspondence with A. G. Meister, who has kindly communicated them to us.*

these elements arise from the necessity of choosing $\mathbf{S}^t_{4\alpha}$ and $\mathbf{S}^t_{5\alpha}$ for all t to lie in the same plane through the symmetry axis as the other $\mathbf{S}^t_{j\alpha}$ (the Wilson **S** vectors for the atom t and the symmetry coordinate $R_{j\alpha}$) and the new values are readily verified. The F matrix elements and the remaining G matrix elements are unchanged.

Following Meister, we have transferred most of the force constants from methylacetylene to methylchloroacetylene. Golton [5] has recalculated the force constants of methylacetylene, taking into account the G matrix changes mentioned above. The potential constants that appear in the F matrix for the A_1 vibration are the same as those of Meister. Of the remainder, k_α, k_β, and $k_{\alpha\beta}$ are not greatly altered, but the change in the value of k_ϕ is considerable. Both sets of values are listed in Table V, together with the set we have adopted for use in the present calculations.

TABLE V

FORCE CONSTANTS FOR METHYLCHLOROACETYLENE (10^5 DYNES/CM.)

	Meister's value	Golton's value	Adopted value
k_H	4.8384	Same	Same
k_c	5.1296	Same	Same
k_a	15.799	Same	Same
k_X	5.3008	Same	Same
k_{ca}	0.47059	Same	Same
$k_{c\gamma}$	−0.26186	Same	Same
k_{Xa}	0	0	0
k_α	0.45342	0.4515	0.4515
k_β	0.56207	0.5636	0.5636
$k_{\alpha\beta}$	0.01285	0.0108	0.0108
k_ϕ	0.12714	0.1524	0.1524
k_θ	0.09729		0.09624
$k_{\phi\theta}$	0.045303		0.05244

It is worth noting that all force constants except k_H, k_X, k_θ, and $k_{\phi\theta}$ have been taken over from methylacetylene. The value of k_H is that calculated by Meister from the frequencies of $\nu_6(e)$ in all three methylhaloacetylenes investigated in the Raman effect by Cleveland and Murray (5); Meister evaluated k_X from the observed frequency of $\nu_2(a_1)$. We have calculated k_θ and $k_{\phi\theta}$ by taking $\nu_9(e)$ = 353 cm.$^{-1}$ and $\nu_{10}(e)$ = 184 cm.$^{-1}$ for $CH_3C{\equiv}CCl$. No frequencies of $CD_3C{\equiv}CCl$ were used to evaluate force constants.

The atomic masses and molecular dimensions used in the calculation were the same as those employed by Meister. The calculated fundamental frequencies, shown in Table VI (second and last columns), are explicit solutions of the fifth power secular equations. Table VI also includes fundamental frequencies calculated by Meister (third column).

ASSIGNMENTS

Fundamentals

With the exception of $\nu_{10}(e)$ all fundamentals in each molecule were observed in either the infrared or Raman spectrum.

The A_1 fundamental bands in the infrared have the doublet structure

[5] *Private communication to the authors.*

TABLE VI

FUNDAMENTAL FREQUENCIES (CM.$^{-1}$)

$CH_3C{\equiv}CCl$				$CD_3C{\equiv}CCl$	
$\nu_{vac.}$ (exp.)**	ν (calc.)	ν (M.)*		$\nu_{vac.}$ (exp.)**	ν (calc.)
2939	2899	2894	$\nu_1(a_1)$	2142	2095
2268	2264	2261	$\nu_2(a_1)$	2252	2266
1380[1]	1385	1391	$\nu_3(a_1)$	1151	1154
1084	1085	1078	$\nu_4(a_1)$	977	977
575	578.5	579	$\nu_5(a_1)$	547	548
2980[2]	3017	3010	$\nu_6(e)$	2235[2]	2257
1453[2]	1453	1456	$\nu_7(e)$	1051[2]	1047
1033[2]	1041	1036	$\nu_8(e)$	825[1]	822
358	353[3]	353[3]	$\nu_9(e)$	343[1]	335
—	184[3]	184[3]	$\nu_{10}(e)$	—	177

*As calculated by Meister.
**Vapor infrared values, unless otherwise noted.
[1] Liquid Raman value.
[2] ν_0 as determined by perpendicular sub-band analysis.
[3] Assumed in order to calculate k_θ, $k_{\phi\theta}$.

characteristic of parallel-type bands of symmetric top molecules, with P–R peak separations approximately as predicted by the Gerhard–Dennison formula (9), viz., 11.2_3 cm.$^{-1}$ for $CH_3C{\equiv}CCl$ and 10.6_7 cm.$^{-1}$ for $CD_3C{\equiv}CCl$. The half widths of the corresponding solution bands are comparatively small ($\sim$8 to 12 cm.$^{-1}$). Likewise, the Raman bands are comparatively sharp, with half widths of the order of 15 cm^{-1}. The depolarization ratios are considerably less than 6/7, except for $\nu_3(a_1)$ in $CD_3C{\equiv}CCl$ which is not strong enough for accurate depolarization measurements.

The spacing between the sub-bands of the doubly degenerate perpendicular fundamental depends on the strength of the Coriolis coupling between degenerate modes. Sub-bands were resolved from one another in $\nu_6(e)$ and $\nu_7(e)$ for both molecules and in $\nu_8(e)$ for $CH_3C{\equiv}CCl$. The latter fundamental was not observed in the vapor spectrum of $CD_3C{\equiv}CCl$, even with a path length of 1 meter. In neither molecule was $\nu_9(e)$ strong enough in the vapor to stand out well among the water bands in the region near 350 cm.$^{-1}$, despite considerable reduction of the water vapor content of the spectrometer by flushing dry nitrogen through a specially constructed housing. In the solution spectra, the perpendicular fundamentals were broad bands with half widths usually greater than 20 cm^{-1}. The Raman bands are likewise comparatively broad with the exception of $\nu_9(e)$. The depolarization ratios which could be measured for the E-type fundamental were found to be 6/7 within experimental error.

It is worth noting that for these molecules the magnitude of the half-band width of the fundamentals appearing in the infrared and Raman spectra of the liquids and solutions provides a criterion for dividing the bands into A_1 and E types. This is true also for the bands in the infrared spectrum of liquid methyl iodide.[6]

The observation by Cleveland Murray (5) of $\nu_{10}(e)$ at 184 cm.$^{-1}$ in the light molecule was approximately confirmed by the frequencies of combination

[6]*As may be seen by examination of the spectra recorded by Irving L. Mador and Ruth S. Quinn (J. Chem. Phys. 20: 1837. 1952).*

bands in which $\nu_{10}(e)$ appears, as is also the calculated value 177 cm.$^{-1}$ for the frequency of this fundamental in the heavy molecule (see below).

The value of $\nu_{10}(e)$ in $CD_3C{\equiv}CCl$ may also be obtained from the Teller–Redlich product rule for the E-type fundamentals (11); viz.,

$$[2] \qquad \nu_{10}(e) = \frac{\prod_{i=6}^{10} \nu_i(e)}{\prod_{i=6}^{9} \nu_i'(e)} \cdot \left(\frac{m_H}{m_D}\right)^{3/2} \cdot \left(\frac{M'}{M}\,\frac{I'_B}{I}\right)^{1/2} = 171 \text{ cm}^{-1}.$$

This value is in good agreement with the values calculated in Table VI and estimated from combination tones. In equation [2] the primed quantities refer to $CD_3C{\equiv}CCl$ and the other symbols have their usual meanings.

The product rule for the fundamentals of the A_1 type is

$$[3] \qquad \prod_{i=1}^{5} \nu_i(a_1) \Big/ \prod_{i=1}^{5} \nu_i'(a_1) = \left(\frac{m_H}{m_D}\,\frac{M'}{M}\right)^{\frac{1}{2}}.$$

The theoretical ratio of the frequencies is 1.946, and the observed value of the left-hand side is 1.930.

COMBINATION AND DIFFERENCE BANDS

$CH_3C{\equiv}CCl$

The remaining bands in the spectra of $CH_3C{\equiv}CCl$ may be readily assigned, as indicated in Tables I and III, on the basis of binary sums or differences. Ternary combinations of the type $\nu_2(a_1)+n\nu_i(e)-n\nu_i(e)$, however, appear to account best for the series of infrared bands lying just below the C≡C stretching fundamental $\nu_2(a_1)$. Meister (14) has made the assignment $[\nu_2(a_1)+\nu_9(e)]-\nu_9(e)$ to the band that occurs on the low frequency side of $\nu_2(a_1)$ in the Raman spectra of 1-chloro, 1-bromo, and 1-iodo acetylene, with $\nu_1(a_1)-2\nu_9(e)$ an alternative assignment. In 1-chloropropyne, however, $\nu_1(a_1)-2\nu_9(e)$ (=2223 cm.$^{-1}$) appears to lie too low to account for any of the strong bands in this region. The band occurring at 2252 cm.$^{-1}$ in the infrared and at 2244 cm.$^{-1}$ in the Raman spectrum is probably $\nu_2(a_1)+\nu_{10}(e)-\nu_{10}(e)$. "Hot" transitions of the form $\nu_2(a_1)+n\nu_i(e)-n\nu_i(e)$ have previously been assigned to bands occurring on the low frequency side of the C≡C stretching fundamental (which corresponds to $\nu_2(a_1)$ in methylchloroacetylene) in the Raman (12) and infrared (4) spectra of methylacetylene.

Fermi resonance with $\nu_5(a_1)$ may account for the high intensity in the infrared spectrum of the band assigned as $\nu_9(e)+\nu_{10}(e)$ (A_1+A_2+E). The fundamental $\nu_7(e)$ gives rise to a very strong overtone (A_1+E) in the infrared, whose intensity is probably enhanced by Fermi interaction with $\nu_1(a_1)$. Similarly, in the Raman spectrum, the $2\nu_7$ band is stronger than the ν_7 band.

Since the strong band at 2749 cm.$^{-1}$ appears to be stronger than the $\nu_3(a_1)$ fundamental, it is more likely to arise from $\nu_1(a_1)-\nu_{10}(e)$ rather than $2\nu_3(a_1)$.

A value of 184 cm.$^{-1}$ for $\nu_{10}(e)$, as mentioned above, appears satisfactory, although examination of the frequencies of the combination and difference

bands in which $\nu_{10}(e)$ occurs suggests that a higher value (190 to 195 cm.$^{-1}$) is to be preferred, at least for the molecule in the vapor.

The assignment of the infrared band at 819 cm.$^{-1}$ is not completely satisfactory.

$CD_3C{\equiv}CCl$

In spite of the presence of strong atmospheric water and solvent absorption, the infrared spectrum of $CD_3C{\equiv}CCl$ appears to show at least three bands below 400 cm^{-1}. Besides $\nu_9(e)$, the binary combinations $[\nu_3(a_1)-\nu_8(e)]$ (E), $2\nu_{10}(e)$ (A_1+E), and $[\nu_5(a_1)-\nu_{10}(e)]$ (E) may occur in this region, and $2\nu_{10}$ has the correct symmetry for resonance with $\nu_9(e)$.

More than one assignment is possible for many of the weaker bands of $CD_3C{\equiv}CCl$. Some of these involve ternary combinations in which $\nu_9(e)$ or $\nu_{10}(e)$ occur. In general, wherever $\nu_9(e)$ occurs in a combination assignment (Table II), an alternative assignment in which $2\nu_{10}(e)$ replaces $\nu_9(e)$ may be made. There appears to be only one band, that at 2318 cm.$^{-1}$ in the infrared spectrum of the vapor, to which may be unequivocally assigned a transition involving $\nu_{10}(e)$. With due regard to anharmonicity the assignment $\nu_1(a_1)+\nu_{10}(e)$ to this band leads to a value of $\nu_{10}(e) > 176$ cm^{-1}. The infrared band at 513 cm.$^{-1}$ gives $\nu_{10}(e) > 170$ cm.$^{-1}$ if assigned to $\nu_9(e)+\nu_{10}(e)$, and $\nu_{10}(e) > 171$ cm.$^{-1}$ if assigned to $3\nu_{10}(e)$. The actual value of $\nu_{10}(e)$ therefore appears to be close to the calculated frequency of 177 cm^{-1}.

There is good evidence for the existence of strong Fermi interaction between $\nu_2(a_1)$ and the band that occurs with a Raman shift of 2302 cm.$^{-1}$ in the liquid and at 2318 cm.$^{-1}$ in the infrared spectrum of the vapor. This band has been assigned to $2\nu_3(a_1)$. In both the Raman and infrared spectra it has an intensity about equal to that of the $\nu_2(a_1)$ fundamental. In the second place, the Raman band is strongly polarized. Thirdly, the experimental value of the frequency of $\nu_2(a_1)$ is lower than would have been expected while that of $2\nu_3(a_1)$ is higher. If one compares, for the data of Table VI, the calculated value of $\delta\nu$, the change in frequency of a fundamental in going from $CH_3C{\equiv}CCl$ to $CD_3C{\equiv}CCl$, with the observed change, one finds that $\delta\nu_{obs.}-\delta\nu_{calc.}$ has values from $+1$ to $+15$ cm.$^{-1}$ for all fundamentals, with the exception of $\nu_2(a_1)$, for which this quantity is -18 cm^{-1}. It therefore seems likely that Fermi interaction has reduced the frequency of the $\nu_2(a_1)$ fundamental by about 20 cm.$^{-1}$, while raising that of $2\nu_3(a_1)$ to about the same extent (observed value of $2\nu_3(a_1)=$ 2318 cm.$^{-1}$ vs. $\nu_3(a_1) = 1151$ cm.$^{-1}$).

Band Contours

The contours of the combination bands in the infrared spectra of the vapors tend to resemble those of the parallel fundamentals, even when the symmetry class of the transition is A_1+E or, as in a few cases, solely E. Possibly a diffused E component would be expected to be less pronounced than an A_1 component of equal intensity, and E bands with large ζ values (see Rotational Structure of Perpendicular Bands, below) take on the appearance of parallel bands under conditions of low resolution. Large ζ_{ij}'s are expected for transitions $\nu_i(a_1)+\nu_j(e)$ in which ζ_j is itself large (3). For both molecules, ζ_9 and ζ_{10} are near

unity (see below). The $CH_3C{\equiv}CCl$ band at 765 cm.$^{-1}$ [$\nu_5(a_1)+\nu_{10}(e)$] shows the type of contour expected under these conditions. The sharpness (for a perpendicular band) of the corresponding band in the solution spectrum may perhaps also be attributed to a large ζ value.

ROTATIONAL STRUCTURE OF THE PERPENDICULAR BANDS

The rotational structure of several of the E-type fundamentals was resolved. The Q-branches of the sub-bands that arise from $\Delta K = +1$, $\Delta J = 0$ transitions are given by

$$[4] \quad \nu_0^{sub} = \nu_0+A'(1-\zeta)^2-B'\pm 2[A'(1-\zeta)-B']K+[(A'-B')-(A''-B'')]K^2$$

which is identical with the expression given by Herzberg (13) except for the factor $(1-\zeta)^2$ instead (4) of $(1-2\zeta)$ which shifts the band origin ν_0 for large ζ. To determine ζ from equation [4], dimensions of the chloropropyne molecule were assumed. Except for the C—Cl bond distance, the dimensions were taken to be the same as those obtained for 1-bromo- and 1-iodo-propyne by Sheridan and Gordy (19); r_{CH} = 1.092 Å, $r_{C\equiv C}$ = 1.207 Å, r_{C-C} = 1.459 Å and $\measuredangle$ HCH = 109°8′. The value of the C—Cl distance was taken to be 1.632 Å, the same as that in chloroacetylene as determined from the microwave spectrum (20). Reciprocal moments are then A'' = 5.281, B'' = 0.075 cm.$^{-1}$ for $CH_3C{\equiv}CCl$ and 2.661 and 0.067 cm.$^{-1}$, respectively, for $CD_3C{\equiv}CCl$.

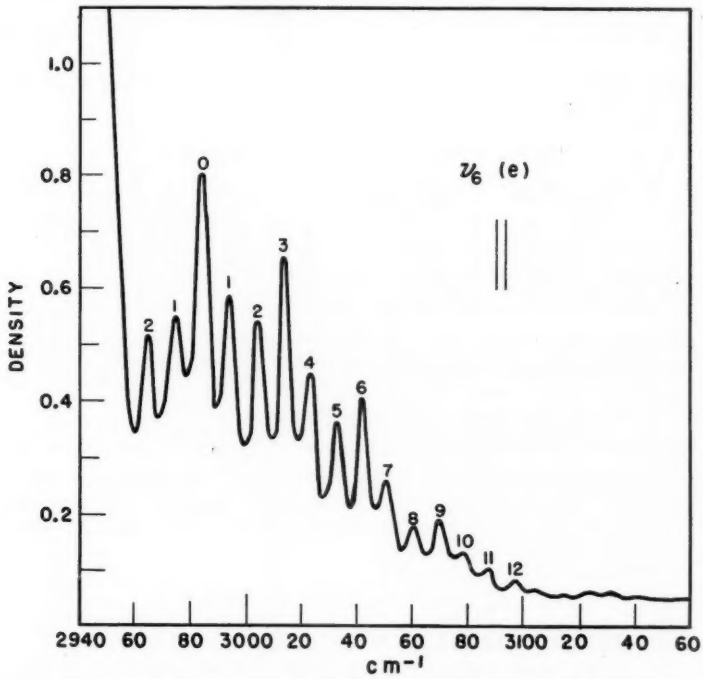


FIG. 4. $\nu_6(e)$ band of $CH_3C{\equiv}C{-}Cl$. The spectral slit width is shown.

In making the K assignments to the sub-bands, one is greatly assisted by the strong, weak, weak, strong, . . . intensity sequence imposed by the nuclear spin of the H (or D) atoms. The strongest peak corresponds to the transition in which K goes from 0 to 1.

The sub-band frequencies observed in $\nu_6(e)$ of $CH_3C{\equiv}CCl$ (Fig. 4) are given in Table VII. The ${}^PQ$ branch for large K's is obscured by $\nu_1(a_1)$. By least

TABLE VII

SUB-BAND FREQUENCIES IN $\nu_6(e)$ OF $CH_3C{\equiv}CCl$

$\nu_{vac.}$, cm.$^{-1}$	Value of K in ${}^PQ_K$	$\nu_{vac.}$, cm.$^{-1}$	Value of K in ${}^RQ_K$
2964.6	2	2984.6	0
2974.8	1	2994.5	1
		3004.3	2
		3014.0	3
		3023.5	4
		3033.2	5
		3042.4	6
		3051.4	7
		3060.7	8
		3070.1	9
		3079.0	10
		3087.5	11
		3096.9	12
		—	
		(3114)	
		(3123)	
		(3131)	

squares the observed peaks have been fitted to equation [4] (with an average deviation of ± 0.13 cm.$^{-1}$) to give

$$[5] \qquad \nu_0^{sub} = 2984.7_0 \pm 9.884\,K - 0.0460\,K^2.$$

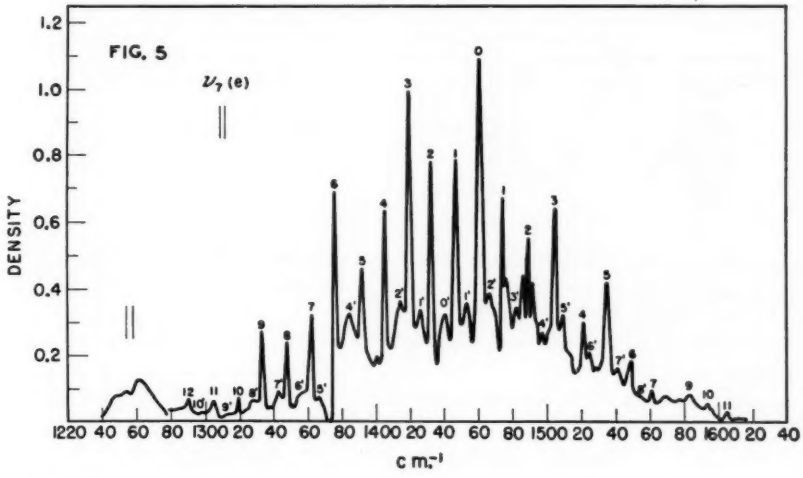
Since $A'' \gg B''$, $(A'-B')-(A''-B'')$ can be set nearly equal to $A'-A''$, whence $A' = 5.235$ cm.$^{-1}$, $B' = B''$, $\nu_0 = 2979.9$ cm.$^{-1}$, and $\zeta_6 = 0.042$.

The intensity distribution among the sub-bands of $\nu_7(e)$ of $CH_3C{\equiv}CCl$ (Fig. 5) permits a choice of either 1419 or 1461 cm.$^{-1}$ for the 0–1 transition. That the latter is probably the correct assignment is shown by the occurrence of the solution peak at 1440 cm^{-1}. Besides the intensity distribution, many of the sub-band frequencies are apparently affected by the presence of overlapping and perturbing bands: $\nu_3(a_1)$ at *ca.* 1395 cm.$^{-1}$, $(\nu_3(e)-\nu_{10}(e))$ (A_1+E) at 1258 cm.$^{-1}$, at least one "hot" transition (see below), and probably a band at about 1510 cm.$^{-1}$ (most likely $(\nu_3(a_1)+\nu_{10}(e))$ (E). The ${}^RQ_K$ sub-bands for K greater than 2 appear to be perturbed, especially in the region between 1500 and 1580 cm^{-1}. The frequencies in Table VIII assigned to ${}^PQ_K$ and ${}^RQ_K$ transitions (the latter up to $K = 2$) may be fitted with a mean deviation of ± 0.3 cm.$^{-1}$ by

$$[6] \qquad \nu_0^{sub} = 1460.81 \pm 13.901\,K - 0.0276\,K^2.$$

Thus $A' = 5.253$ cm.$^{-1}$, $\nu_0 = 1453.78$ cm.$^{-1}$, and $\zeta_7 = -0.337$.

$\nu_8(e)$ (Fig. 6) is a comparatively weak band, with most of the ${}^RQ$ sub-bands obscured by $\nu_4(a_1)$ and some irregularity in the ${}^PQ$ spacings (see Table IX).



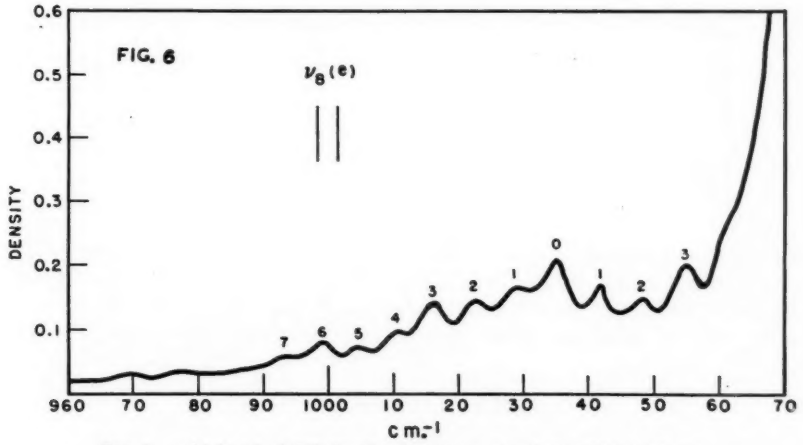


FIG. 5. $\nu_7(e)$ band of $CH_3C{\equiv}C{-}Cl$. The spectral slit width is shown.
FIG. 6. $\nu_8(e)$ band of $CH_3C{\equiv}C{-}Cl$. The spectral slit width is shown.

TABLE VIII

SUB-BAND FREQUENCIES IN $\nu_7(e)$ OF $CH_3C{\equiv}CCl$

$\nu_{vac.}$, cm.$^{-1}$	K in ^PQ_K	$\nu_{vac.}$, cm.$^{-1}$	K in ^RQ_K
1290.1	12	1460.7	0
1304.8	11	1474.7	1
1319.0	10	1489.1	2
1333.1	9	1505.2	3
1347.6	8	1521.2	4
1362.3	7	1535.0	5
1375.7	6	1548.2	6
1391.6	5	1560.8	7
1405.1	4	—	8
1418.7	3	1583.0	9
1432.1	2	1593.3	10
1446.8	1	1604.6	11

TABLE IX

SUB-BAND FREQUENCIES IN $\nu_8(e)$ OF $CH_3C{\equiv}CCl$

$\nu_{vac.}$, cm.$^{-1}$	K in ^PQ_K	$\nu_{vac.}$, cm.$^{-1}$	K in ^RQ_K
992.5	7	1035.0	0
998.8	6	1041.4	1
1004.0	5	1048.0	2
1010.2	4	1054.7	3
1016.1	3		
1022.2	2		
1028.7	1		

In it, with the rotational constants assumed the same in the ground and excited states, ζ_8 was determined from the average spacing (excluding $^PQ_7$ and $^PQ_6$) to be 0.40 and $\nu_0 = 1034.5$ cm^{-1}.

In neither $CH_3C{\equiv}CCl$ nor $CD_3C{\equiv}CCl$ was the structure of $\nu_9(e)$ or $\nu_{10}(e)$ resolved.

The sub-bands (Table X) on the high frequency side of $\nu_6(e)$ in $CD_3C{\equiv}CCl$

TABLE X

SUB-BAND FREQUENCIES IN $\nu_6(e)$ OF $CD_3C{\equiv}CCl$

$\nu_{vac.}$, cm.$^{-1}$	K in ^PQ_K	$\nu_{vac.}$, cm.$^{-1}$	K in ^RQ_K
2192.2	10	2237.9	0
2197.0	9	2242.0	1
2201.6	8	2245.9	2
2206.1	7	2249.7	3
2210.4	6		
2214.9	5		
2219.5	4		
2223.8	3		
2228.6	2		
2233.8	1		

(Fig. 7) are obscured by $\nu_2(a_1)$. The intensity distribution in the rest of the band makes it uncertain whether $^RQ_0$ is 2224 or 2238 cm^{-1}. Since the solution frequency (here 2229 cm.$^{-1}$) is ordinarily lower than that of the vapor band center, $^RQ_0$ is probably 2238 cm^{-1}. By least squares (average deviation ± 0.4 cm.$^{-1}$),

$$[7] \qquad \nu_0^{sub} = 2237.41 \pm 4.619\,K + 0.01385\,K^2,$$

with the result that $A' = 2.675$ cm.$^{-1}$, $\zeta_6 = 0.112$, and $\nu_0 = 2235.3_7$ cm^{-1}.

Frequencies in the $\nu_7(e)$ band (Fig. 8) are shown in Table XI. Two spurious

TABLE XI

SUB-BAND FREQUENCIES IN $\nu_7(e)$ OF $CD_3C{\equiv}CCl$

$\nu_{vac.}$, cm.$^{-1}$	K in ^PQ_K	$\nu_{vac.}$, cm.$^{-1}$	K in ^RQ_K
997.8	8	1056.5	0
1004.8	7	1063.6	1
1012.1	6	1070.7	2
1019.3	5	1078.1	3
1026.5	4	1085.2	4
1033.8	3	1093.0	5
1041.3	2	1100.2	6
1048.8	1	(1102.6)*	
		1108.0	7
		(1111.6)*	

**Spurious to this band (see text).*

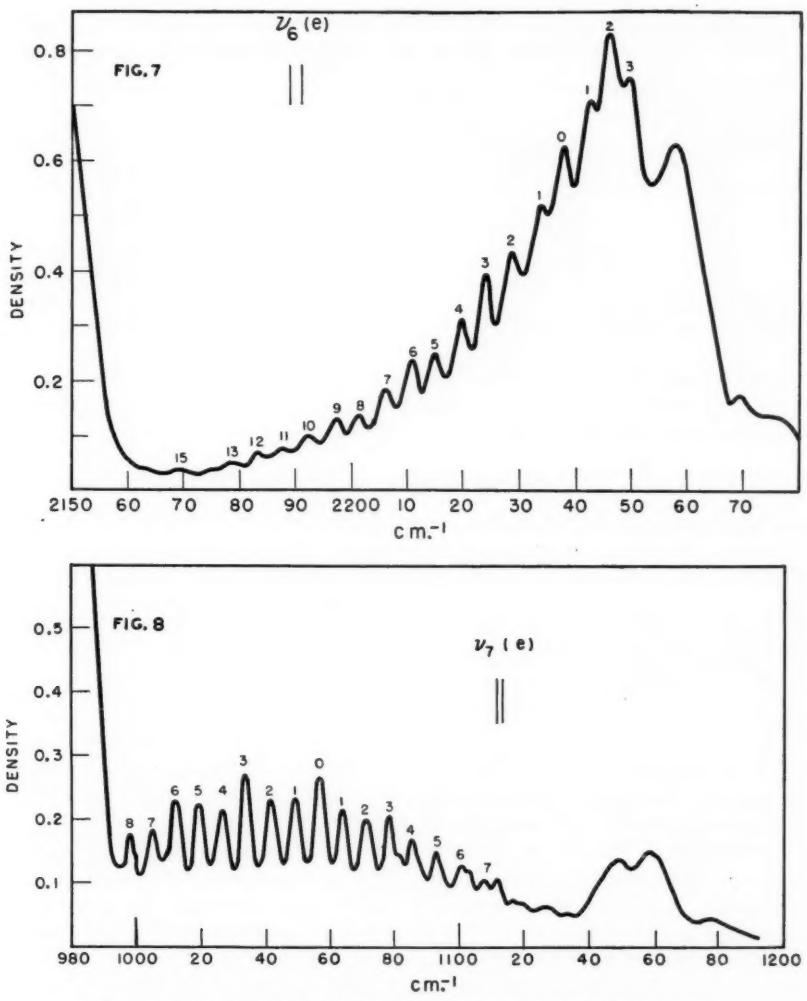


FIG. 7. $\nu_6(e)$ band of $CD_3C{\equiv}C{-}Cl$. The spectral slit width is shown.
FIG. 8. $\nu_7(e)$ band of $CD_3C{\equiv}C{-}Cl$. The spectral slit width is shown.

peaks appear at 1103 and 1112 cm^{-1}. These have been attributed (see Assignments) to the parallel contour of a combination band. The remaining subbands are expressed (with an average deviation of ± 0.16 cm.$^{-1}$) by

$$[8] \qquad \nu_0^{\text{sub}} = 1056.00 \pm 7.361\,K + 0.0049\,K^2$$

with $A' = 2.666$ cm.$^{-1}$, $\nu_0 = 1050.8$ cm.$^{-1}$, and $\zeta_7 = -0.406$.

Table XII summarizes the ζ's and compares them with the values obtained for the corresponding vibrations in $CH_3C{\equiv}C{-}H_3$ and in $CH_3C{\equiv}C{-}D_{10}$.

As in the present case, the structure of the $\nu_9(e)$ and $\nu_{10}(e)$ bands in these molecules was not resolved. Boyd and Longuet-Higgins (3) have shown

TABLE XII

SUMMARY OF ζ'S

	$CH_3C{\equiv}CCl$	$CD_3C{\equiv}CCl$	$CH_3C{\equiv}CH$[1]	$CH_3C{\equiv}CD$[2]
$\zeta_6(e)$	0.042	0.112	0.074	0.071
$\zeta_7(e)$	−0.357	−0.406	−0.39	−0.37
$\zeta_8(e)$	0.40		0.387	0.40
$\zeta_9(e)$	$0.90 < \zeta < 1$		$0.96 < \zeta < 1$	$0.92 < \zeta < 1$
$\zeta_{10}(e)$	$0.90 < \zeta < 1$		$0.96 < \zeta < 1$	$0.92 < \zeta < 1$

[1]*Boyd–Thompson results.*
[2]*Grisenthwaite–Thompson results.*

generally that the sum rule for the ζ's of C_{nv} molecules, when there are n equivalent atoms symmetrically disposed about the symmetry axis and only one degenerate symmetry class E, is

$$[9] \qquad \sum_i \zeta_i = (\text{no. of axial atoms}) - 2 + B/2A,$$

to a first order approximation. For $CH_3C{\equiv}CCl$

$$[10] \qquad \zeta_9 + \zeta_{10} = 1.90_2,$$

which places each of the individual ζ values between 0.90 and 1. The corresponding range in methylacetylene is 0.96 to 1. For $CD_3C{\equiv}CCl$, where only ζ_6 and ζ_7 have been determined:

$$[11] \qquad \zeta_8 + \zeta_9 + \zeta_{10} = 2.30_7,$$

which is consistent with a value of ζ_8 not far from 0.4 and ζ_9 and ζ_{10} again near unity. The signs and magnitudes of the ζ's for chloropropyne are similar to those observed for similar degenerate vibrations in other molecules.[7]

In addition to the strong features in the $\nu_7(e)$ band of $CH_3C{\equiv}CCl$, there appear a large number of weak subsidiary peaks interspersed between the $\nu_7(e)$ peaks. Although the presence of water absorption and the occurrence of the doublet contour of $\nu_3(a_1)$ around 1400 cm.$^{-1}$ introduce uncertainties into the values of the frequencies, an attempt has been made to fit them by equation [4]. Eighteen of the twenty-four subsidiary peaks listed in Table XIII and shown in Fig. 5 can be fitted with success; the remainder, in the region of 1500 cm.$^{-1}$, may arise from other "hot" bands or from the effects of water absorption. The $\nu_7(e)$ sub-bands at 1535 cm.$^{-1}$ show an irregular intensity, and it and other features in this region may be associated with the presence of a weak solution band near 1510 cm^{-1}. The equation resulting from the assignment shown in Table XIII, viz.,

[7]*A rough empirical correlation may be seen between ζ values and vibrational type, as shown, for example, by the similarity in ζ's for corresponding vibrations in methylacetylene and chloromethylacetylene (Table XII). For CH_3CN and CH_3NC, where there is only one low-lying perpendicular bending mode, the ζ's are 0.068, −0.45, 0.42, and 0.99, and 0.08, −0.33, 0.36, and 0.92 respectively (Thompson, H. W. and Williams, R. L. Trans. Faraday Soc. 48: 502. 1952). In $H_3BC{=}O$, $\zeta_1 = 0.13$ and $\zeta_3 = 0.56$ (Cowan, R. D. J. Chem. Phys. 18: 1101. 1950).*

TABLE XIII

SUBSIDIARY PEAKS IN REGION OF $\nu_7(e)$ OF $CH_3C{\equiv}CCl$
(Most peaks approximate)

$\nu_{vac.}$, cm.$^{-1}$	Tentative K in ^PQ_K of hot band	$\nu_{vac.}$, cm.$^{-1}$	Tentative K in ^RQ_K of hot band
1297.7	10	1440.1	0
1312.5	9	1453.7	1
1328.7	8	1466.7	2
1341.8	7	1476.8	
1355	6	1482.0	3
1366.9	5	1491.8	
1384.1	4	1494.4	
1400.1	3	1497	4
1414.1	2	1500	
1425.8	1	1509.7	5
		1512.9	
		1524.8	6
		1529	
		1540.5	7
		1554.5	8

[12] $$\nu_0^{sub} = 1440.0 \pm 14.06\,K + 0.015\,K^2,$$

gives $A' = 5.296$ cm.$^{-1}$, $\nu_0 = 1430.5$ cm.$^{-1}$, and $\zeta = -0.34$ with much less accuracy than before. The K assignment is uncertain, since the intensity alternation is not clear, and it may be that the band origin should be shifted by one or more peaks. The solution spectrum shows a weak shoulder located at about 1428 cm^{-1}. Although the ν_0 value is therefore doubtful, the value of ζ will not be greatly dependent upon the assignment. It is, within experimental limits, identical with the value of ζ for $\nu_7(e)$, as is to be expected for a transition of the type $\nu_7(e)+n\nu_i(e)-n\nu_i(e)$. Our resolving power was not great enough to make the presence of hot bands in conjunction with other strong perpendicular fundamentals observable.

With the exception of the "hot" bands mentioned above, no combination band showed sufficiently well-defined perpendicular structure to make possible an estimation of ζ.

DISCUSSION

There are two aspects of the isotope effect on the vibrational spectrum of these molecules which require emphasis. Firstly there is a shift in frequency of the $\nu_5(a_1)$ band of 28 cm.$^{-1}$ which seems too large to anticipate for a C—Cl valence vibration so far removed from the C atom where isotopic substitution took place.[8] Secondly, this band doubles in intensity in the Raman effect on deuterium substitution and the $\nu_9(e)$ band for example is enhanced in intensity by about a factor of 3 whereas smaller intensity changes are observed for these bands in the infrared spectra. It is readily noticed that there is no simple relation between the observed intensities of corresponding Raman bands of $CD_3C{\equiv}CCl$ and $CH_3C{\equiv}CCl$. Nor do the intensities of the corresponding infrared bands of $CD_3C{\equiv}CCl$ and $CH_3C{\equiv}CCl$ change in any simple manner. However, for isotopic substitution Crawford has developed a sum rule (7)

[8] *The isotopic shift of the C—Cl vibration in CH_3Cl and CD_3Cl is 37 cm.$^{-1}$, cf. Ref. (11), page 315.*

which is applicable to the sum of I/ν^2 for the infrared bands and the sum of $S/\Delta\nu^2$ for the Raman bands of the A_1 modes. Unfortunately the measurement of both the infrared and Raman intensities of these modes is complicated by the fact that several bands overlap, by contributions from bands in Fermi resonance, and by uncertainty in placing the background for the Raman bands at $\sim$2925 cm^{-1}. The experimental errors introduced by these difficulties make it impossible to test quantitatively the validity of the intensity sum rules for these molecules.

The large changes in Raman intensity of corresponding bands of these molecules are probably due to the fact that here the molecular polarizability varies in a complicated manner with the normal coordinate whereas in 1-chloropropane, the saturated analogue of 1-chloropropyne, the intensity of the C—Cl mode for example is given approximately by polarizability changes in the C—Cl bond.

The necessity of dealing with the molecular polarizability in $CH_3C{\equiv}CCl$ rather than bond polarizabilities is further indicated by the presence of the abnormally short CH_3—C and C—Cl bonds in this molecule showing that strong interactions exist between all pairs of bonds between axial atoms. The explanation for the short C—Cl bond in $HC{\equiv}C$—Cl has been given (18) in terms of resonance with the doubly bonded form $H\bar{C}{=}C{=}\overset{+}{Cl}$, whereas hyperconjugation has been involved to account for the short C—C bond in $CH_3C{\equiv}CH$ (6). Thus a realistic potential function for this type of molecule should include non-negligible interaction constants between adjacent bonds. Meister's function (14) for 1-chloropropyne might be criticized on these grounds since the C≡C, CCl interaction constant (K_{Xa}) is taken as zero.[9] However since the agreement between observed and calculated frequencies for $CH_3C{\equiv}CCl$ is quite good it must mean that the K_{Xa} interaction has been taken up in the values for the other constants. In this connection it is instructive to inspect the sets of force constants that Meister has tested for $CH_3C{\equiv}CBr$ (14). They are all about equally good from the point of view of closeness of fit between calculated and observed frequencies, yet one set differs from the others essentially by having a fairly large (0.65×10^5 dynes per cm.) value for the C≡C, CBr interaction constant. The resulting adjustment necessary in the other constants is only to change $K_{C{\equiv}C}$ by about 4%, K_{CCl} by about 8%, with minor changes in two interaction constants.

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MESYL* DERIVATIVES OF HYDRAZINE[1]

By Alan G. Newcombe[2]

ABSTRACT

Monomesylhydrazide, 1-acetyl,2-mesylhydrazide, and *sym*-dimesylhydrazide were obtained by means of the Schotten–Baumann reaction. For comparison with these compounds the hydrazinium dimesylate, hydrazinium monomesylate, monomesylhydrazide mesylate, and monoacetylhydrazide mesylate were prepared. The preparation of dimesyldiimide by the action of metallic sodium on N,N-dichloromesylamide was attempted.

INTRODUCTION

Although numerous hydrazides of aromatic and aliphatic carboxylic acids have been prepared, very little is known of the hydrazides of sulphonic acids. The few sulphonic acid hydrazides which have been prepared were chiefly derivatives of aromatic sulphonic acids. It seemed, therefore, of interest to ascertain whether aliphatic sulphonic acid hydrazides could be prepared.† Because of the ready availability of mesyl chloride the hydrazine derivatives of methanesulphonic acid were investigated first.

It was found that few of the reactions available for the preparation of the hydrazides of carboxylic acids can be used for the synthesis of the hydrazides of aromatic or aliphatic sulphonic acids. Curtius and Lorenzen (4) found that by treating hydrazine with either the anhydride or the ethyl ester of benzenesulphonic acid the hydrazine disulphonate salt, and not the *sym*-dibenzenesulphonylhydrazide, was formed. Similar results were obtained in this laboratory using the corresponding aliphatic sulphonic acid derivative (mesyl anhydride (1) or ethyl mesylate (1)) in attempts to prepare the *sym*-dimesylhydrazide.

Raschig's (16) method for the preparation of hydrazodisulphonic acid ($HO—SO_2—NH—NH—SO_2—OH$) was also found to be unsuitable for the preparation of the *sym*-dimesylhydrazide when mesyl chloride was used as the sulphonating agent. Very small quantities of *sym*-dimesylhydrazide were obtained, however, by using the method of Diels and Paquin (8), substituting mesyl chloride for the chloromethyl carbonate.

Considerably better, although still low, yields of *sym*-dimesylhydrazide were obtained by means of the Schotten–Baumann reaction under the conditions reported by Helferich *et al.* (10, 12) for the preparation of dimesylimide.

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**The use of the word mesyl, which was first suggested by Helferich and Gnüchtel (11), in place of methanesulphonyl is followed throughout this paper.*

†G. H. Stempel, Can. Patent No. 511,584, April 5, 1955, reports the preparation of aliphatic monosulphonylhydrazides by the use of the Schotten–Baumann reaction utilizing alkyl sulphonyl halides having at least four carbon atoms.

Several changes in the procedure were made in order to increase the yield, but were unsuccessful.

Analysis of the material produced by the Schotten–Baumann reaction gave figures that agreed well with those calculated for *sym*-dimesylhydrazide. It was realized, however, that the reaction product might have been hydrazinium dimesylate, hydrazinium monomesylate, monomesylhydrazide mesylate, hydrazinium dimethanesulphinate,‡ or 1,1-dimesylhydrazide, since these materials possess similar or identical analytical figures. The possibility of the Schotten–Baumann product being identical with one of the first three compounds named was ruled out by comparing it with hydrazinium dimesylate, hydrazinium monomesylate, and monomesylhydrazide mesylate prepared by reliable methods (2). Since the Schotten–Baumann product did not react with benzaldehyde under conditions which resulted in the immediate formation of benzalmesylhydrazone and benzalazine from monomesylhydrazide hydrochloride and hydrazinium dimesylate, respectively, it could not have been hydrazinium dimethanesulphinate or 1,1-dimesylhydrazide.

In a similar manner it was shown that the Schotten–Baumann reaction of acetylhydrazide with mesyl chloride yielded the 1-acetyl,2-mesylhydrazide and not acetylhydrazide mesylate, acetylhydrazide methanesulphinate, or 1-acetyl,1-mesylhydrazide.

In attempting to prepare a monosubstituted hydrazide, namely the monomesylhydrazide, the methods for the preparation of the monohydrazides of carboxylic acids were investigated first. Following the method of Curtius and Struve (5) by heating the methane sulphonamide with hydrazine hydrate or anhydrous hydrazine yielded only the unchanged starting material. Heating the ethyl or butyl (14) mesylate with hydrazine hydrate or anhydrous hydrazine following the method of Curtius and Hofmann (3) yielded in every case the undesired hydrazinium monomesylate. These results are in line with those obtained by Curtius and Lorenzen (4) in their attempts to prepare the monobenzenesulphonylhydrazide. The monomesylhydrazide was readily obtained, and in excellent yield, by means of the Schotten–Baumann reaction. The monomesylhydrazide, a viscous oil, gave a solid hydrochloride and on treatment with benzaldehyde immediately formed the benzalmesylhydrazone.

It was thought that the diacylhydrazides (*sym*-dimesylhydrazide and 1-acetyl,2-mesylhydrazide) might be useful starting materials in the preparation of dimesyldiimide and acetylmesyldiimide. The preparation of these substances by the oxidation of the hydrazides with fuming nitric acid according to Diels *et al.* (7, 8) proved unsuccessful. The method of Stollé (17) was found not to be feasible since the mercury salts of *sym*-dimesylhydrazide and 1-acetyl,2-mesylhydrazide decomposed too readily to permit their isolation. Attempts to prepare the diimide derivatives by oxidation of the disubstituted hydrazides by means of lead tetraacetate in glacial acetic acid were also unsuccessful. While no reaction occurred with 1-acetyl,2-mesylhydrazide at either 0°, 25°, or the boiling point of the solution, the *sym*-dimesylhydrazide

‡*Dann and Davies (6) have shown that the production of sulphinate salts from hydrazine and sulphonic acid chlorides occurs rather easily.*

reacted vigorously, even in the cold, with the evolution of a gas and complete decomposition of the hydrazide. The oxidation of the similar diacetylhydrazide (*sym*) with lead tetraacetate in glacial acetic acid gave a reddish colored oil in a yield of 33% which, like the "diacetyl diimide" of Stollé(17) and Inhoffen, Pommer, and Bohlman (13), decomposed too rapidly to permit analysis.

Finally the possibility of preparing the dimesyldiimide via the action of sodium metal on a N,N-dihalomesylamide was investigated. For this purpose the unknown N,N-dichloromesylamide was prepared by the action of sodium hypochlorite on an aqueous solution of mesylamide at 0°. The N,N-dichloromesylamide was obtained in a pure state and a high yield. While this investigation was in progress Mel'nikov, Sukhareva, and Kavenoki (15) reported the preparation of N,N-dichloromesylamide by the same procedure. The bromination of mesylamide with sodium hypobromite gave a product which lost bromine on washing with ether or other organic solvents.

When a suspension of N,N-dichloromesylamide in ether or benzene was treated with sodium wire and the solvent removed, an orange colored mixture was obtained from which, however, no dimesyldiimide could be isolated.

EXPERIMENTAL

sym-Dimesylhydrazide

To an ice-cold solution of 5.48 gm. (80 mM.) of hydrazine hydrochloride in 10 ml. of water, 20.9 gm. (182 mM.) of mesyl chloride and 60.5 ml. of 4.34 *N* sodium hydroxide solution were added dropwise and at such a rate that the pH of the solution was in the proximity of 8.0. During the addition, which in general required 30 min., the temperature of the solution was kept at 6°. The stirring of the mixture was continued for 15 min. after the addition was completed. At the end of this time hydrochloric acid was added and the solid was filtered off, washed with water, and dried *in vacuo*. The dimesylhydrazide was obtained in yields ranging from 8 to 12%; m.p. 168.5–170° (with decomposition). Calc. for $C_2H_8O_4N_2S_2$ (186.2): C, 12.8; H, 4.25; N, 14.9; S, 34.05%. Found: C, 12.8; H, 4.21; N, 15.2; S, 33.80%.

Variations.—Using, instead of the 4.34 *N* sodium hydroxide, 2 *N* sodium hydroxide, 2 *N* potassium hydroxide, saturated barium hydroxide, or sodium bicarbonate solution, or adding the mesyl chloride at a faster rate did not improve the yield of the *sym*-dimesylhydrazide.

Hydrazinium Dimesylate

A solution containing 9.61 gm. (100 mM.) of methanesulphonic acid, dissolved in 10 ml. of water, was prepared and cooled to 0°. The solution was then added slowly to 2.5 gm. (50 mM.) of hydrazine hydrate. The resultant solution, on standing overnight at 6°, produced a crystalline precipitate, which was filtered off and air dried. Concentrating the mother liquor *in vacuo* yielded more material. The total yield of hydrazinium dimesylate was 8.31 gm. (74%). The material, after drying *in vacuo* at 100° to constant weight, melted at 202–203°. *Analyses*: Calc. for $C_2H_{12}O_6S_2N_2$ (224.3): C, 10.71; H, 5.39; N, 12.50; S, 28.59%. Found: C, 10.97; H, 5.29; N, 12.48; S, 28.89%.

The hydrazinium dimesylate was recovered unchanged by recrystallization

from 99% ethanol. On recrystallization from 95% ethanol only hydrazinium monomesylate, melting at 143.0–143.5°, was obtained. The decomposition of a hydrazine di-salt to the corresponding mono-salt is not uncommon (9).

Hydrazinium Monomesylate

To an ice-cold mixture of 5.0 gm. (100 mM.) of hydrazine hydrate and 22 ml. of ether in a flask equipped with a reflux condenser, was added slowly 9.61 gm. (100 mM.) of methanesulphonic acid. After the exothermic reaction ceased the ether was distilled off, and the white residue was recrystallized from a small amount of ethanol. The material thus obtained melted from 139 to 144°. For further purification it was dissolved in a small volume of hot water and precipitated by the addition of 99% ethanol to the point of turbidity; m.p. 143.0–143.5°. Calc. for $CH_8O_3SN_2$ (128.2): C, 9.37; H, 6.29; N, 21.85%. Found: C, 9.42; H, 6.46; N, 21.74%.

Monomesylhydrazide

A solution of 5.0 gm. (100 mM.) of hydrazine hydrate in 15 ml. of water was placed in a three-necked flask immersed in a salt–ice bath. To the solution, 11.5 gm. (100 mM.) of mesyl chloride and 50 ml. of a 2 *N* sodium hydroxide solution were added dropwise and with stirring in such a manner that the temperature did not rise above 8°. After the addition had been completed the solution was concentrated *in vacuo* with the occasional removal of sodium chloride. To the concentrate was added 99% ethanol and the solution again was concentrated *in vacuo*. The residue was taken up in anhydrous ether, centrifuged, and the solvent removed *in vacuo*. The residue, a clear, colorless, viscous oil weighed 10.31 gm. (93.5%). The monomesylhydrazide is moderately soluble in alcohol or ether; but readily soluble in chloroform or carbon tetrachloride. *Analyses*: Calc. for $CH_6O_2N_2S$ (110.1): C, 10.9; H, 5.50; N, 25.4%. Found: C, 10.7; H, 5.25; N, 25.1%.

Monomesylhydrazide Hydrochloride

The mesylation of 5.0 gm. (100 mM.) of hydrazine hydrate was carried out as described above. To the reaction mixture was added 25 ml. of concentrated hydrochloric acid, and the *sym*-dimesylhydrazide which was formed in a small amount was filtered off. The filtrate was concentrated *in vacuo*. The white residue was recrystallized twice from boiling 99% ethanol. The crystals of monomesylhydrazide hydrochloride, after drying *in vacuo*, weighed 10.79 gm. (73.7%) and melted at 152–153°. *Analyses*: Calc. for $CH_7O_2N_2SCl$ (146.6): C, 8.20; H, 4.82; N, 19.14%. Found: C, 8.24; H, 5.20; N, 19.21%.

Monomesylhydrazide Mesylate

This salt of monomesylhydrazide was best prepared by the following method. A solution of 1.10 gm. (10 mM.) of monomesylhydrazide in 10 ml. of water was added to a solution of 0.96 gm. (10 mM.) of methanesulphonic acid in 30 ml. of water and the mixture was concentrated *in vacuo*. The oil was dissolved in 99% ethanol and the solution again concentrated *in vacuo*. This operation was repeated once more. The white crystalline substance was recrystallized, after solution in a warm mixture of 20 ml. of 99% ethanol and

2 ml. of chloroform, by the addition of anhydrous ether to the point of turbidity. The substance (m.p. 137–138°) was recrystallized once more using a warm mixture of chloroform: absolute ethanol (1:1 v/v) and anhydrous ether. In this manner 0.24 gm. (11.7%) of the monomesylhydrazide mesylate was obtained; m.p. 144–145°. *Analyses*: Calc. for $C_2H_{10}O_5N_2S_2$ (206.2): C, 11.63; H, 4.88; N, 13.59%. Found: C, 11.43; H, 5.08; N, 13.67%.

Benzal Mesylhydrazone

A solution of 1.10 gm. (10 mM.) of monomesylhydrazide in 16 ml. of water was added to a solution of 1.06 gm. (10 mM.) of benzaldehyde in 30 ml. of hot 95% ethanol. The mixture was heated to the boiling point and alcohol was added until the precipitate was dissolved. The yellow precipitate which formed on cooling was filtered off, redissolved in hot ethanol, and precipitated by the addition of water. The colorless crystals were once more recrystallized from warm ethanol and water. The benzal mesylhydrazone weighed 1.11 gm. (56%); m.p. 150–151°. *Analyses*: Calc. for $C_8H_{10}O_2N_2S$ (198.2): C, 48.5; H, 5.07; N, 14.13%. Found: C, 48.4; H, 5.10; N, 14.19%.

1-*Acetyl*,2-*mesylhydrazide*

Acetylhydrazide was obtained by the method of Curtius and Hofmann (3) and mesylated in the following manner.

To a cooled solution of 5.0 gm. (67.5 mM.) of acetylhydrazide in 10 ml. of water were added dropwise and with gentle stirring 7.75 gm. (67.5 mM.) of mesyl chloride and 34 ml. of 2 *N* sodium hydroxide at such a rate that the pH was kept below 8.0. The temperature of the mixture was not allowed to rise above 8°. Towards the end of the addition the 1-acetyl,2-mesylhydrazide, a fine white crystalline solid, precipitated. The solid was collected with suction on a Büchner funnel, washed with a small volume of water, and dried *in vacuo*. Yield: 2.27 gm. (22.2%); m.p. 197–199°. *Analyses*: Calc. for $C_3H_8O_3N_2S$ (152.2): C, 23.65; H, 5.29; N, 18.40%. Found: C, 23.59; H, 5.22; N, 18.28%.

Acetylhydrazide Mesylate

To a solution of 0.77 gm. (6.8 mM.) of 95% methanesulphonic acid in 30 ml. of water was added a solution of 0.50 gm. (6.8 mM.) of acetylhydrazide in 4 ml. of water, and the mixture was concentrated *in vacuo*. The sirupy residue was taken up in 99% ethanol and the solvent removed *in vacuo*. This process was repeated twice using anhydrous ether followed by 99% ethanol. The dry material was then recrystallized from warm 99% ethanol by the addition of anhydrous ether. The acetylhydrazide mesylate was thus obtained in a yield of 1.06 gm. (90%), m.p. 114–116°. *Analyses*: Calc. for $C_3H_{10}O_4N_2S$ (170.2): C, 21.20; H, 5.92; N, 16.47%. Found: C, 21.10; H, 6.09; N, 16.35%.

Reactivity of Hydrazine Derivatives with Benzaldehyde

Hydrazinium Salts

To a solution of 5 mM. of hydrazinium monomesylate or hydrazinium dimesylate and equivalent amounts of sodium acetate in 2.2 ml. of water was

added 10 mM. of freshly distilled benzaldehyde. In each case, the formation of the well-known benzalazine took place immediately.

Monoacylhydrazide Salts

To a solution of acetylhydrazide mesylate (0.447 gm., 2.63 mM.) and 0.292 gm. (3.56 mM.) of anhydrous sodium acetate in 5 ml. of water was added 0.279 gm. (2.63 mM.) of benzaldehyde and the mixture was well shaken. The known benzalacetylhydrazone was formed.

In a similar experiment with monomesylhydrazide hydrochloride (2.63 mM.), but using 80% acetic acid as solvent (10 ml.), the known benzalmesylhydrazone was obtained.

Diacylhydrazides

Neither the 1-acetyl, 2-mesylhydrazide nor the *sym*-dimesylhydrazide reacted with benzaldehyde under conditions similar to the one immediately above. Both hydrazides were recovered unchanged.

N,N-Dichloromesylamide

To a solution of 0.64 gm. (16 mM.) of sodium hydroxide in 3.5 ml. of water cooled in ice was added 0.76 gm. (8 mM.) of mesylamide, and chlorine gas was passed through the solution for a period of 15 min. The white precipitate which formed immediately was filtered off, washed with a small amount of water, and dried *in vacuo*. The N,N-dichloromesylamide was obtained in a yield of 1.09 gm. (83.2%); m.p. 84–86°. Carbon, hydrogen, and nitrogen analyses were attempted but the substance exploded in the combustion tube. Iodometric analysis indicated a positive chlorine content of 43.1%. Theory, 43.2%.

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THE APPLICATION OF GAS–LIQUID PARTITION CHROMATOGRAPHY TO PROBLEMS IN CHEMICAL KINETICS[1]

By A. B. Callear[2] and R. J. Cvetanović

ABSTRACT

A gas–liquid partition chromatographic method for analysis of samples of the order of magnitude of a micromole is described. Examples of application are given.

INTRODUCTION

The analysis of 'liquid products', produced for example in photochemical reactions, has in the past been attempted by mass spectrometer analysis, by infrared analysis, and by specific tests for various functional groups. The liquid products are most frequently complex mixtures and in usual chemical kinetic investigations appear in quantities varying from a fraction to several micromoles. Their analysis has great significance for elucidating the mechanism of the process. Owing to the small size of the samples and their complexity, a complete mass spectrometric analysis can rarely be carried out. Other methods of analysis usually lead to an incomplete picture of the reaction products. The present paper describes the application of gas–liquid partition chromatography to these and some related problems.

Two types of gas chromatography have been considered in connection with the present problem: the displacement method (3, 7, 11) and the gas–liquid partition method (4, 5, 6). In the former, the mixture to be analyzed was first adsorbed on charcoal in a column, and was then displaced from the column by nitrogen containing a material such as bromobenzene or ethyl acetate. Separation occurred as a result of the difference in adsorption energies. In the latter method the stationary phase used was Celite 545 (kieselguhr) mixed with a liquid of low vapor pressure (silicones, liquid paraffin, glycerol, dinonyl phthalate, and others). The gases were eluted from the column with nitrogen, and separation occurred as a result of the different partition coefficients between the gas and liquid. This method was first used for the separation of organic acids (5) and amines (4, 6) and the analyzer was an automatic burette. Later Ray (12, 13) developed a more general method using thermal conductivity cells as the analyzer. He analyzed samples of about 10 mgm. and used a 6 ft. column containing 0.45 gm. dinonyl phthalate per gram of celite.

In the present work the partition method has been chosen for analysis of liquid products in preference to the displacement method because the same column can be used indefinitely and there is no contamination of the components with the displacing compound. There are also, in individual cases, the advantages of reversibility and greater selectivity. The method of Ray is

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further developed in order to make it applicable to the extremely small quantities of material produced in chemical kinetic studies. The details of a gas–liquid partition chromatographic apparatus applicable to samples of the order of magnitude of a micromole are given with particular emphasis on a discussion of the factors of importance for its construction and use. Some examples of application are given. In some favorable cases as little as 2×10^{-9} moles of a gas can be detected. In general, the sensitivity is of the order of 1×10^{-8} moles and is, therefore, at least as good as that of a gas burette or of a mass spectrometer. Isolation of fractions from relatively large samples has been previously reported (7, 8). The possibility of the isolation of fractions from the extremely small samples used in the present work has been investigated and it has been found that chromatographic fractionation can be combined, with distinct advantage, with other analytical procedures. This is especially true in cases when the peaks overlap and some of the constituents cannot be isolated singly. The method has proved applicable both for quantitative analysis and for identification of components of unknown mixtures.

SENSITIVITY OF THE THERMAL CONDUCTIVITY MEASUREMENTS

The possibility of application of gas–liquid partition chromatography to the extremely small amounts of products encountered in kinetic studies depends on a high sensitivity of detection of these products in very large amounts of the eluent gas. Thermal conductivity measurements appear to be, at present, the most convenient means of achieving the necessary sensitivity, provided that a high sensitivity can be obtained while the general "noise" level is kept low. A number of factors affect both the sensitivity and the stability of thermal conductivity measuring devices.

In the present work two thermal conductivity cells, forming in the customary manner the adjacent arms of a Wheatstone bridge, were used. They were, however, both placed at the exit end of the column and separated from each other by a series of cold traps so that the substances eluted from the column affected only the first cell while pure eluent gas passed through the second cell. For the measurement of very small amounts of substances this arrangement was preferred to the usual one, with the "reference" cell preceding the column, because of the difficulty of completely eliminating fluctuations in the input pressure of the eluent gas. The bridge was balanced with the eluent gas alone in both cells. The temperature change of the platinum resistance wire in the conductivity cell due to the presence of an impurity is proportional to V^2, the square of the e.m.f. across the wire. A given resistance change of the wire produces an off-balance signal proportional to V. The sensitivity, i.e., the off-balance signal arising from the presence of a fixed percentage of an impurity, is, therefore, proportional to V^3. A very marked increase in sensitivity can, evidently, be achieved by increasing the e.m.f. across the resistance wire. However, it was found that if the wire temperature was increased to over 200°C., a permanent change in the zero position occurred at every peak, indicating either a physical change in the surface of the wire or a change of its position within the cell. The former would alter the tempera-

ture discontinuity (14) at the gas–solid interface and thus change the zero point. The platinum wires were actually maintained at about 100°C., as was established by observing resistance change with wattage dissipation. At the flow rates used, no appreciable difference in the wire temperature could be observed for stationary and flowing gas.

Platinum resistance wire of 10^{-3} in. diameter was used for the conductivity cells. Since the desired sensitivity was achieved, no experiments with different thicknesses of the wire were conducted. Thinner wires may offer some advantage in the greater response, but are more difficult to handle and in all probability would be more sensitive to pressure fluctuations because of greater temperature discontinuity.

The effect of an impurity on the thermal conductivity of a gas is given by Chapman and Cowling (1) for a special molecular model. If the impurity has a very high molecular weight compared to the bulk of the gas, this equation reduces to

$$\lambda(\text{impure mixture}) = \lambda - n_{21}\lambda^2(5-4B)/2F$$

where λ is the thermal conductivity of the pure gas, B is a constant and, under these conditions, F is inversely proportional to the molecular weight of the impurity. n_{21} is the ratio of the number of impurity molecules to the number of eluent gas molecules. Thus for this ideal case, the effect of a constant amount of impurity is proportional to the square of the thermal conductivity of the eluent gas and proportional to the first power of the molecular weight of the impurity. Though the practical case will only approximate to this relationship, it is clear that a gas of high thermal conductivity should be used. For this reason, hydrogen has been chosen for the eluent gas in preference to nitrogen. The use of hydrogen as eluent gas has recently been reported by Patton, Lewis, and Kaye (10).

A rough comparison of the performance of hydrogen and nitrogen gas eluents can be made. The thermal conductivity ratio is about 7 to 1. The changes in thermal conductivity of the gases on addition of the same percentage of a vapor of high molecular weight differ by at least a factor of 7 and possibly by a factor as high as 7^2. If the wire is to be at 100°C. for both gases, the ratio of the e.m.f.'s is $7^{1/2}$. It follows that the off-balance signal produced by the impurity in the nitrogen is between $7^{3/2}$ and $7^{5/2}$ times less than that for hydrogen. The small fluctuations in temperature between the two thermal conductivity cells would produce a "noise" $7^{1/2}$ times greater for hydrogen than for nitrogen, since the voltage is that much higher. Thus the ratios of signal to noise for the two cases would differ by a factor between 7 and 7^2 in favor of hydrogen. Apart from this fundamental difference in behavior, to obtain the same size "peak" for both gases on the recording chart, the amplification has to be very much higher for nitrogen, introducing further electrical noise and noise due to pressure variations, making stable working conditions more difficult to achieve.

Since each molecule of an impurity present in the eluent gas can be regarded as making its own contribution to the recorded peak and this contribution

is proportional to the time each molecule remains in the thermal conductivity cell, it can be expected that the area under the peaks should decrease with increasing rate of eluent gas flow. A marked variation in peak area with flow rate has been observed with the experimental arrangement used, though the flow rates were not known sufficiently accurately to establish a quantitative relationship.

GENERAL FEATURES OF THE APPARATUS AND THE PROCEDURE

The flow system is shown in Fig. 1. Hydrogen gas from a cylinder and reducing valves enters the apparatus at *A* at a pressure slightly greater than one atmosphere as regulated by the small buffer volume *B* (200 cc.) and the

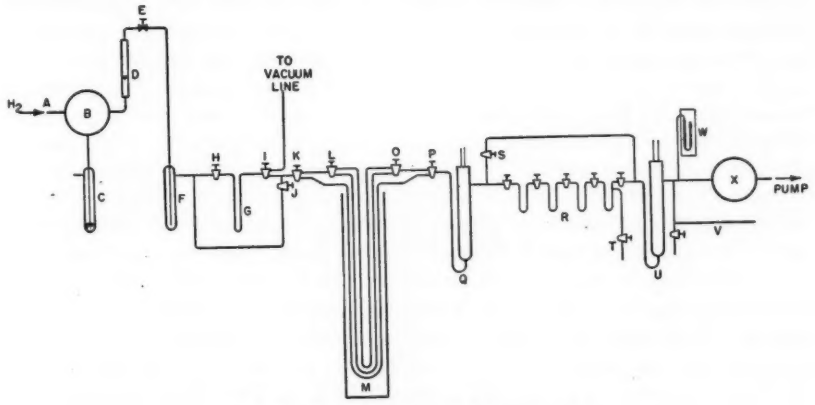

FIG. 1. General outlay of the apparatus.

bubbler *C* containing dibutyl phthalate. Through the latter, excess gas is allowed to bubble at a constant rate. The rotameter *D* gives an approximate value for the rate of flow and a polythene diaphragm valve *E* can be used to vary the pressure applied to the column. The liquid nitrogen trap *F* removes any condensable impurities from the hydrogen. The sampling trap *G* can be evacuated by closing the vacuum stopcock *H* and opening the two-way capillary vacuum stopcock *I* to the vacuum manifold. The sample is measured in a gas burette and is condensed in *G*, care being taken to raise finally the level of liquid nitrogen above the condensed sample. During introduction of sample, the hydrogen bypasses *G* by means of stopcock *J*. To introduce the sample to the column, *I* is closed and *H* is slowly opened to disturb the pressure as little as possible. With *G* full of hydrogen at one atmosphere, *I* is opened to the column and *J* is closed. It is usually necessary to pass hydrogen for a few minutes to restore stability of the analyzer. The sample is then evaporated into the gas stream by replacing the liquid nitrogen with hot water. The present apparatus incorporates three columns for different types of separation. The column is selected by operation of three-way capillary vacuum stopcocks *K*, *L*, *O*, and *P*. The sample passes through the column *M* which is contained

in a 6.5 cm. i.d. glass cylinder about 100 cm. long. A spiral of resistance wire placed inside the cylinder is used to heat the column to the desired temperature, as measured on a thermometer near the center of the cylinder. The 'dead space' between *G* and *M* is reduced as much as possible by using capillary tubing. After leaving *M*, the gas passes through about 20 cm. of 4 mm. i.d. thin-walled glass tubing, so that it is cooled to room temperature before entering the first thermal conductivity cell *Q*. After passing through *Q*, the sample can be removed from the hydrogen in a series of cold traps *R*, made of 4 mm. i.d. thin-walled glass tubing. The volume is kept as small as possible by using capillary stopcocks between the traps. The various components passing through the first thermal conductivity cell are recorded automatically in the form of peaks. They can usually be trapped out in successive liquid nitrogen traps *R* on the first run. In the case of an unknown mixture which gives overlapping peaks, it is sometimes necessary to observe the chromatographic spectrum on the first run and then send the sample through again, in order to effect the most favorable fractionation. The last trap is connected through stopcock *T* to the vacuum system so that the fractions can be successively removed and measured. While this is done the stream of hydrogen is bypassed through *S*. After the second thermal conductivity cell *U* the gas stream enters a 15 liter flask, serving as a buffer volume, and is then pumped out by a vacuum oil pump. The pressure is observed on the manometer *W*, and is maintained constant by bleeding in air through the $\frac{1}{2}$ mm. i.d. glass capillary tubing *V*. In some experiments the pressure was 40 mm. and in others 70 mm. Variations in pressure between these values had little effect on the separations. The flow rates were determined by observing the time taken for a small amount of air to pass between *Q* and *U*. The volume of the tubing and traps between *Q* and *U* was known. The flow rates in cc. (N.T.P.) per min. were

Column 1: 1.8; Column 2: 15.3; Column 3: 3.3.

CONSTRUCTION OF THE THERMAL CONDUCTIVITY CELLS

Fig. 2 shows one of the thermal conductivity cells. The gas enters the cell through the 4 mm. i.d. thin-walled glass tubing *A*. The platinum wire *FG*

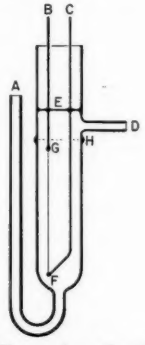

FIG. 2. Thermal conductivity cell.

(10^{-3} in. in diameter) is silver soldered to thick platinum crosspieces which, in turn, are silver soldered to tungsten rods *B* and *C*. Spot welded contacts used originally were found to be unsatisfactory. The tungsten leads are protected from the thermostatting water by extension of the 15 mm. i.d. glass tube of which the cell is made some 10 cm. above the seal *E*. The wire is mounted by breaking the cell at *H* and sealing back on when the wire has been attached. The gas exit is at *D*. The two cells are embedded side by side in paraffin wax contained in a glass cylinder 10 cm. in diameter. The whole is in a two liter beaker containing water which is stirred. The paraffin wax extends to *E* and the water level is about 5 cm. above this. A layer of oil is spread on the surface of the water to prevent evaporation. In early experiments, the inner cylinder contained mercury instead of paraffin wax. The performance was poor, becoming worse when the mercury was stirred. A gel was used successfully until, after a few weeks, it began to decompose and liquefy when it was replaced with paraffin wax.

The platinum wires formed two adjacent arms of a Wheatstone bridge network, the junction of the two wires being connected to the amplifier and the other ends of the wires to a 12 volt battery. A box of oil-immersed resistances formed the other arms of the bridge. In series with the battery was a 30 ohm resistance. All the connections in the bridge network were made with thick copper wire. The off-balance signal was amplified with a d-c. amplifier (Liston-Becker Model 14) and the output was fed to a pen recorder. Screening of the circuit was not necessary. The amplifier was not used on full gain and its "noise" level was far below that arising from temperature fluctuations between the two thermal conductivity cells. The resistance of the platinum wires was about 12 ohms at room temperature.

CONSTRUCTION AND EXPERIMENTS WITH DIFFERENT TYPES OF COLUMNS

A number of different columns were made and their performance with synthetic samples observed. In order to maintain the flow rates within suitable limits, columns of relatively small diameters were used. The dinonyl phthalate columns were $2\frac{1}{4}$ mm. i.d. glass capillary tubing, and the glycerol column was 4 mm. i.d. glass tubing. They were made in *U* shape, each arm of the *U* being 3 ft. They were filled by attaching small funnels to the open ends and the stationary phase was packed in by prolonged tapping of the curved portion on a solid floor. The packing was improved by heating the column to 100°C. during this operation, and seemed to result in a uniformly packed column. It was found that a certain amount of tailing was exhibited by the peaks as smaller and smaller samples were used. The following experiments were all carried out with a mixture of methyl and ethyl alcohol in order to test the separation and the tailing of the peaks with different column materials. (*a*) Since it has been suggested that the tailing occurs as a result of some adsorption on the solid (5), some columns were made containing celite which had been stirred in a solution of 10% dinonyl phthalate in methyl alcohol and acetone. The resulting solid was drained on a Büchner funnel and most of the alcohol and acetone was removed by drawing air through it. The resulting

column contained 4 gm. dinonyl phthalate to 10 gm. of celite. This treatment did not reduce the tailing of the peaks. (*b*) Varying amounts of sorbitol tristearate were added, in order to block the surface with strongly adsorbed polyfunctional groups. This had little effect. (*c*) Instead of celite some weaker adsorbents were tried as supporting materials. Oxidized copper spheres (200–325 mesh) proved unsatisfactory, as did powdered teflon. Glass spheres (passing 270 mesh) on the other hand proved to be advantageous from the point of view of tailing and the uniformity of column packing. Larger glass spheres were tried but were less successful. The glass spheres contained some iron oxide and attempts were made to remove this in aqua regia followed by washing with distilled water. Columns made from glass spheres prepared in this way gave very little separation of the two alcohols. The untreated glass spheres gave the most satisfactory columns. They were mixed with 4% dinonyl phthalate by weight in a beaker, and the resulting mixture packed uniformly and tightly into the glass tubing. As a result a suitable, relatively slow flow rate was obtained. Most of the work described below was carried out on columns constructed in this way. (*d*) It was found that addition of phosphoric acid to the columns reduced the tailing of organic acids (5). Addition of phosphoric acid to the dinonyl phthalate glass columns caused complete removal of alcohols, possibly through formation of non-volatile esters. This type of column might have use for some special problems, where small amounts of material are to be separated from an excess of alcohol. The three columns that were finally integrated into the apparatus were : (1) 1 part dinonyl phthalate and 25 parts glass spheres passing 270 mesh; (2) 20 parts of celite and 9 parts of dinonyl phthalate; (3) 1 part of glycerol and 100 parts glass spheres passing 270 mesh. Column 2 is used for the less volatile mixtures since it gives a higher flow rate. Column 3 has not yet been used to advantage since the separations have been successfully carried out on the dinonyl phthalate columns.

THE EFFECT OF TEMPERATURE ON SEPARATION

In a theoretical treatment of gas–liquid partition chromatography, James and Martin (5) have defined the retention volume of a substance as the product of the flow rate and the appearance time of the center of the peak. Both of these quantities are dependent on the pressures at the inlet and outlet of the column and if these pressures are varied, the retention volume changes. In the present work it was found more convenient to consider the appearance times rather than the less direct quantities, the retention volumes.

The results of James and Martin and later of Ray (12) showed that the appearance times of successive members of a homologous series are mutually related in a simple manner. Ray pointed out that separation of a mixture is impaired if the temperature of the column is too high. This was confirmed in the present work when it was shown that a sample of 10^{-6} mole of a mixture of methanol and ethanol gave overlapping peaks at 70°C. while a good separation was effected at room temperature. It was found to be of advantage in a number of cases to carry out separation of the more volatile components at

room temperature and to start heating the column part way through the experiment in order to avoid excessive appearance times for the less volatile components.

EXAMPLES OF APPLICATION

Liquid products formed by reaction of oxygen atoms with ethylene, reaction of oxygen atoms with acetaldehyde, and decomposition of ethylene oxide in the presence of ethylene have been analyzed by the present method in order to test its applicability. The details and kinetics of these reactions are given elsewhere (2). The detection of impurities in an ethylene cylinder was also carried out, since in some chemical reactions the ethylene gave rise to abnormal behavior.

Since aldehydes are important products in the reaction of oxygen atoms with ethylene, as well as in a large number of other reactions, experiments were carried out using synthetic mixtures of acetaldehyde, propionaldehyde, and butyraldehyde. Fig. 3*a* shows the separation obtained on column 1 at

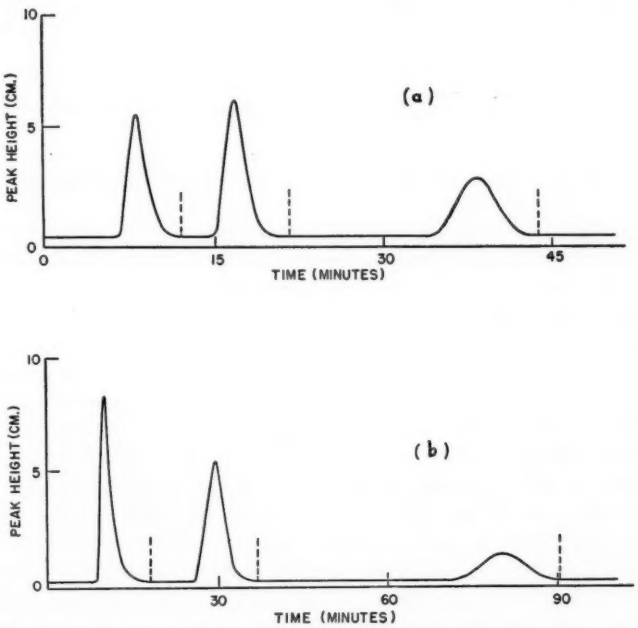

FIG. 3. (*a*) Chromatogram of a synthetic mixture of acetaldehyde, propionaldehyde, and butyraldehyde. (*b*) Chromatogram of −80°C. fraction from the reaction of O-atoms with ethylene.

50°C. The compounds were trapped out at points shown by the vertical dotted lines. Each component was measured before and after recovery with a gas burette, on a volume of 2.85 cc. Each burette reading on this quantity could be in error by 2%.

	Burette reading (pressure in mm. Hg)	
	Introduced	Recovered
Acetaldehyde	10.9	11.5
Propionaldehyde	13.6	13.7
Butyraldehyde	8.5	8.3

Fig. 4 shows the variation in peak height for acetone, with the size of the sample, demonstrating the linearity of the recording device, and the reproducibility of the method.

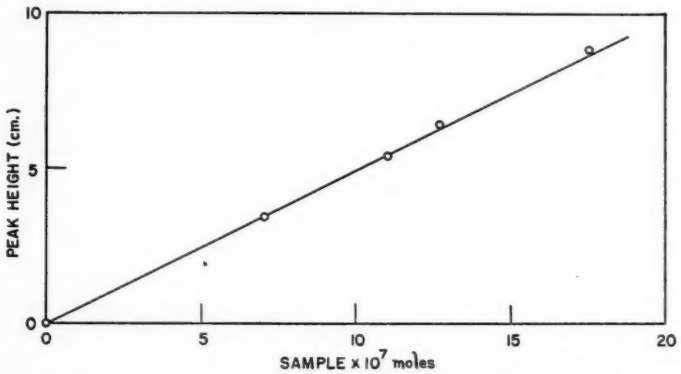

FIG. 4. Variation of peak height with varying amounts of acetone.

Fig. 3*b* shows the chromatogram obtained at 26°C. from the −80°C. Le Roy still (9) fraction from the oxygen atom and ethylene reaction. The peaks were trapped out and mass spectrometric analysis identified the first as acetaldehyde, the second as propionaldehyde, and the third as largely butyraldehyde. The rest of the third peak could have been accounted for as some compound isomeric with butyraldehyde. It was shown that under identical conditions methyl ethyl ketone separated only partially from the butyraldehyde. In another experiment, the third peak was split by trapping at the maximum point. The two halves had the same mass spectrum. With the column at 26°C. instead of 50°C. as used on the synthetic mixture of aldehydes, the ratio of the appearance times of the higher aldehydes to lower aldehydes has increased and the separation has considerably improved.

Fig. 5*a* shows the chromatogram obtained from the −80°C. fraction from the reaction of oxygen atoms and acetaldehyde carried out on column 1 at 26°C. The peaks were trapped out and identified by the mass spectrometer. The heater was switched on after 75 min. and the temperature of the column was 85°C. at the appearance of the third peak. The first peak is the excess acetaldehyde, the second peak is acetone, and the third is biacetyl. The acetone was present to the extent of 3% of the acetaldehyde. It is doubtful if it could have been identified by any conventional method since although the parent peak of the acetone would be observed in such a mixture on the mass spectrometer, the rest of the spectrum would be masked. As a check a

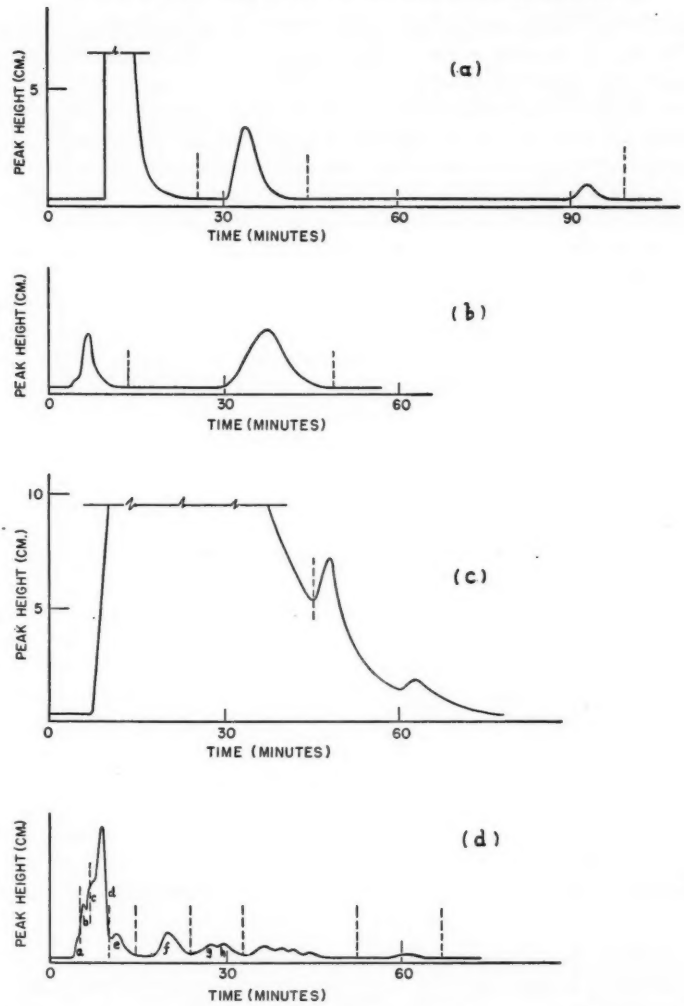

FIG. 5. (*a*) Chromatogram of −80°C. fraction from the reaction of O-atoms with acetaldehyde. (*b*) Chromatogram of room temperature fraction. (*c*) Chromatogram of −80°C. fraction from the mercury sensitized decomposition of ethylene oxide in the presence of small amounts of ethylene. (*d*) Chromatogram of the impurities in cylinder ethylene gas.

synthetic mixture of 30 parts of acetaldehyde and 1 part of acetone was run on the column and the same appearance times were observed. Fig. 5*b* shows the room temperature fraction from the same reaction separated on column 2 at 26°C. The peaks were trapped out and measured and analyzed as water and biacetyl. A sample of water was passed through the column and the position of the first peak was verified.

Fig. 5*c* shows the chromatogram of the −80°C. fraction obtained on column 1 at 26°C. for the decomposition of ethylene oxide in the presence of ethylene. The heater was switched on after 29 min. The sample was 1.5×10^{-3} moles consisting mainly of ethylene oxide which, in such a large quantity, appeared to saturate the column. The two small peaks on the tail of the ethylene oxide peak were trapped out as shown by the vertical line. At the appearance of the third peak the temperature was 102°C. The sample obtained from the tail of the ethylene oxide peak was rechromatographed and gave three separate peaks. The first was ethylene oxide, the second butyraldehyde, and the third pentaldehyde.

Fig. 5*d* shows the chromatogram obtained for the −60°C. fraction from a cylinder of ethylene prepared by dehydration of ethyl alcohol. Four hundred milliliters of impure ethylene at one atmosphere were condensed on a Le Roy still. The ethylene was removed at −175°C. and the −60°C. fraction yielded 1.04×10^{-5} moles of impurity. The chromatogram was started at 26°C. and the heater was switched on after 24 min. By trapping out according to the vertical lines, the impurities were identified by mass spectrometric analysis as (*a*) CO_2, (*b*) propylene, (*c*) isobutane, (*d*) butene-2, (*e*) isopentane, (*f*) diethyl ether and pentene-2, (*g*) hexane, (*h*) hexene (branched chain). The rest of the spectrum consisted of heptenes, heptanes, octenes, and octanes. No ethyl alcohol was detected.

The foregoing examples illustrate the applicability of the gas–liquid partition chromatography to the very small samples encountered, for example, in chemical kinetic and photochemical investigations. Good reversibility of the gas–liquid partition process is demonstrated by the observed quantitative recovery of the aldehydes. It should be mentioned at the same time that with the small samples used in the present work some compounds exhibit a partially irreversible adsorption. In some instances the reversibility is strongly temperature dependent. Thus, water and biacetyl show incomplete recoveries, especially at lower column temperatures. It is, therefore, necessary, when quantitative determinations are made, to establish the percentage recovery for each compound in the mixture at a particular column temperature.

ACKNOWLEDGMENT

Applicability of gas–liquid partition chromatography to chemical kinetic problems is being independently investigated in these laboratories by Dr. K. O. Kutschke and the authors are pleased to acknowledge some useful exchange of information and discussion. The authors are also thankful to Drs. J. E. Currah and R. R. Barefoot of Canadian Industries Ltd., McMasterville, P.Q., for some general information on the subject, to Dr. A. Tickner for mass spectrometer analysis, and to Mr. L. C. Doyle for valuable technical assistance.

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A NOTE ON THE ALKALOIDS OF *BUPHANE DISTICHA*

By L. G. Humber and W. I. Taylor

In the course of work which has been discontinued we had occasion to examine the alkaloidal content of some bulbs of *Buphane disticha* Herb. (*Haemanthus toxicarius* Herb.) and our results differ somewhat from those recorded by Tutin (8) and Lewin (4). The crude alkaloids were chromatographed over activated alumina to furnish in low yield lycorine (previously isolated by Tutin) and a new base which does not appear to have been characterized previously. The base, m.p. 189°, analyzed for $C_{17}H_{19}O_4N$, had one methoxyl, no N-methyl, one active hydrogen, and one readily hydrogenatable double bond which from infrared data must be trisubstituted. The infrared spectra of the free base and its perchlorate showed that the double bond could not be $\alpha\beta$ to the nitrogen atom. It gave a positive test for a methylenedioxy group with Labat's reagent and the ultraviolet spectrum (λ_{max} 285 mμ, log ϵ 3.2) suggested the presence of the aromatic moiety shown in (I) since it closely resembled safrole (5). The double bond was not conjugated with the aromatic nucleus since the ultraviolet absorption spectrum of the dihydro-compound was identical to that of the original base. The active hydrogen was present in a hydroxyl group since the dihydro-base gave an O-acetate (ν_{CO} 1710 cm.$^{-1}$) rather than a N-acetyl derivative. The nature of the hydroxyl group has not been determined but it is unlikely to be tertiary since it acetylated readily; however in an attempted chromic acid oxidation of the dihydro-compound only the starting material could be isolated in 50% yield.

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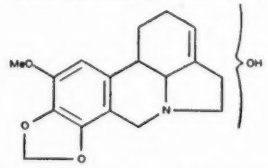

If this alkaloid resembles other members of this class of known constitution, e.g. lycorine (2, 7), homolycorine (3), and lycorenine (3), then the above results are compatible with the formula (I). The lack of material precludes further study at this time but we have shown by direct comparison and infrared spectra that our new base is not identical with crinamine, m.p. 193–194° (6), or haemanthamine, m.p. 200° (1), both of which have the formula $C_{17}H_{19}O_4N$ and contain a methylenedioxy and a methoxyl group.

EXPERIMENTAL[1]

Dried shredded bulbs of *Buphane disticha* (1500 gm.) were percolated with 95% alcohol (48 liters). The combined extracts were concentrated to dryness

[1]*All melting points are uncorrected and the infrared spectra are measured in potassium bromide mulls.*

and the residue triturated with dilute hydrochloric acid. The acid solution after several washings with chloroform was basified and the precipitated alkaloids taken up in chloroform. The dried extract on concentration afforded the crude bases (4.3 gm.) which were chromatographed over activated alumina (300 gm.). Most of the material was irreversibly adsorbed but a chloroform eluate (850 mgm.) and an ethanolic eluate (250 mgm.) were obtained.

Lycorine

In ethanol the ethanolic eluate slowly deposited needles (75 mgm.), m.p. 260°, which gave an undepressed melting point on admixture with an authentic sample of lycorine. Found: C, 66.9; H, 6.0. Calc. for $C_{16}H_{17}O_4N$: C, 66.9; H, 5.9%.

The Base

The chloroform eluate in ethanol slowly gave the base in large prisms (350 mgm.), m.p. 189°, unchanged on further crystallization. Found: C, 67.8; H, 6.4; N, 4.7; OMe, 10.6; act. H (Zerewitinow), 0.35. Calc. for $C_{17}H_{19}O_4N$: C, 67.7; H, 6.3; N, 4.7; OMe, 10.3; act. H, 0.33%. In microhydrogenation 4.6 mgm. took up 0.37 ml. (N.T.P.) and the theoretical for one double bond requires 0.35 ml. (N.T.P.). The ultraviolet absorption spectrum measured in 95% ethanol showed a maximum 285 mμ (log ε 3.17) and a minimum 260 mμ (log ε 2.59) and was unaltered in acidic or alkaline solution. The base gave a positive test for a methylenedioxy group with Labat's reagent.

Base Perchlorate

The salt was crystallized from water, m.p. 119°. Found: C, 47.6; H, 5.5. Calc. for $C_{17}H_{19}O_4N.HClO_4.1.5H_2O$: C, 47.5; H, 5.5%.

Dihydro-base

The base was hydrogenated in acetic acid using platinum oxide as a catalyst. The dihydro derivative had m.p. 200°, from acetone. Found: C, 67.3; H, 7.0. Calc. for $C_{17}H_{21}O_4N$: C, 67.3; H, 7.0%. The ultraviolet absorption spectrum showed a maximum at 285 mμ (log ε 3.2), and in the infrared the medium strength band present at 840 $cm.^{-1}$ in the original base had disappeared.

Monoacetyldihydro-base Perchlorate

The dihydro-base (50 mgm.) was acetylated in acetic anhydride (2 ml.) using a drop of perchloric acid as a catalyst. The free base after isolation could not be obtained crystalline and was converted into its perchlorate, which crystallized readily from water, m.p. 131–132°. Found on a sample dried at 60° for 12 hr. *in vacuo*: C, 45.8; H, 5.8. Calc. for $C_{19}H_{23}O_5N.HClO_4.3H_2O$: C, 45.6; H, 6.0%. The infrared showed ν_{CO} at 1710 cm^{-1}.

ACKNOWLEDGMENTS

We are indebted to the National Research Council of Canada for support and to Dr. S. Uyeo for a sample of crinamine and Dr. Hans-G. Boit for the haemanthamine. We thank Mr. W. Fulmor and Staff of Lederle Laboratories Division of American Cyanamid for the determination of the infrared spectra.

The *Buphane disticha* was obtained in the Belgian Congo through the facilities afforded by the Institut National pour L'Etude Agronomique at Keyburg.

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THE VIBRATIONAL SPECTRUM OF THE SULPHITE ION IN SODIUM SULPHITE[1]

BY J. C. EVANS[2] AND H. J. BERNSTEIN

The Raman and infrared spectra of the sulphite ion in sodium sulphite have been reinvestigated. Hibben (3), on reviewing the work done prior to 1939, decided that the Raman spectrum of the sulphite ion required further examination. More recently, Siebert (7) has obtained the Raman spectra, without measuring the depolarization ratios, of aqueous solutions of three sulphites and has assigned the four bands observed in each spectrum to the four fundamental modes of the ion. In the infrared, Miller and Wilkins (4) included several sulphites in their study of the absorption spectra of solid salts, but confined their study to the region 3–16 μ. We have shown that measurement of the depolarization ratios of the Raman bands and an examination of the infrared spectrum between 3 and 33 μ confirm Siebert's assignment.

Two samples of sodium sulphite which gave identical spectra were examined. One was made available to us by Professor H. G. Thode and the other was C.P. grade (Fischer Scientific Company). The Raman spectrum of a saturated aqueous solution was obtained with a White photoelectric recording spectrometer (8), and depolarization ratios were measured (1) and corrected (5). A Perkin Elmer double-pass infrared spectrometer with LiF, NaCl, KBr, CsBr optics was used to obtain the infrared spectra of a saturated aqueous solution and of solid films of the sulphite. Nujol films and films obtained by evaporating aqueous solutions on AgCl were examined.

The results are tabulated in Table I. In some regions in the infrared, absorption by water or nujol made examination difficult or impossible.

X-Ray diffraction results (9) indicate that the sulphite ion is pyramidal (C_{3v}) with the sulphur atom at the apex. This model should have two sym-

[1]*Issued as N.R.C. No. 3619.*
[2]*National Research Council Postdoctorate Fellow, 1953–55.*

TABLE I

Assignment		Raman, aqueous solution			Infrared	
		cm.$^{-1}$	ρ_{obs}	ρ_{true}	Aqueous solution	Solid
$2\nu_1$	A	—			—	1995 (vw)
$\nu_1 + \nu_3$	E	—			—	1968 (vw)
$2\nu_3$	$A + E$	—			—	1932 (vw) 1912
$2\nu_2$	A	—			—	1213 (w)
$\nu_2 + \nu_4$	E	—			—	1135 (w)
ν_1	a	967 (s)	0.64	0.47	1002 (m)	1010 (m)
ν_3	e	933 (m)	1.05	0.86	954 (s)	961 (s)
$2\nu_4$	$A + E$	896 (vw)	?		—	—
ν_2	a	620 (w)	P		632 (w)	633 (s)
ν_4	e	469 (m)	1.06	0.86	—	496 (s)

metric modes of vibration ν_1 and ν_2 (a type) and two asymmetric doubly degenerate modes ν_3 and ν_4 (e type). All four modes are infrared and Raman active.

The observed Raman spectrum is immediately explained in terms of the four expected fundamental vibrations. The strong polarized Raman band at 967 cm.$^{-1}$ is assigned to ν_1, the symmetric stretching mode, while the other polarized weak band at 620 cm.$^{-1}$ is assigned to ν_2. The two depolarized bands of medium intensity at 933 and 469 cm.$^{-1}$ are assigned to ν_3 and ν_4 respectively. The remaining very weak band at 896 cm.$^{-1}$ may be 2 ν_4.

The infrared spectrum of the aqueous solution shows three bands which must be identified as ν_1, ν_2, and ν_3. ν_4 was not observed, the absorption of the water in this region being strong. The large discrepancies between the positions of the Raman and infrared bands must be ascribed to the strong intermolecular interaction, and, as is usually found in such cases, the infrared bands have higher frequencies (6).

The infrared spectrum of the solid shows several bands that are satisfactorily explained as combinations and overtones of the four fundamental modes.

Using the mean values of the Raman and infrared frequencies of the four modes in aqueous solution, the dimensions of the ion from X-ray data, and the equations derived from a four-constant potential function (2), the following values of the four constants were calculated: $K_1 = 5.49_6$, $K_1' = 0.64_3$, $K_\delta = 1.01_9$, and $K_\delta' = 0.31_0$ all in units of 10^5 dynes per cm. These constants were used to calculate the following frequencies of the fundamentals in the isotopic ion $S^{34}O_3^{16}$: $\nu_1 = 972$, $\nu_2 = 623$, $\nu_3 = 937$, and $\nu_4 = 457$, all in cm.$^{-1}$.

We wish to thank Professor H. G. Thode for suggesting this problem.

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AN OSCILLOSCOPIC POLAROGRAPH

BY G. F. ATKINSON AND W. A. E. MCBRYDE

Polarographic half-wave potentials may be determined without the necessity of obtaining the whole polarographic wave by the use of several derivative techniques. Many of these are based on the introduction of a low-voltage alternating signal into the cell circuit, and observation of some change produced in this signal by its passage through the cell. We have extended the designs of Müller *et al.* (4) and Boeke and van Suchtelen (1) for an oscilloscopic polarograph (*i*) by the introduction of phase-shifting components so as to produce elliptical Lissajous patterns, and (*ii*) by the incorporation of an electronic switch in the oscilloscope's vertical input so as to provide a reference signal in addition to that observed for the polarographic cell. Since the apparatus was built we became aware of the circuit of Rodrequez and Sancho (5) which incorporates the first of the above features. As this type of determination requires the recognition of a distorted pattern on the oscilloscope screen, discrimination is made much easier by the presence of a second undistorted pattern at the same time, especially as the two images may be superimposed.

The circuit is shown in Fig. 1. The cell circuit proper, in which the polarizing direct current flows, is made up of the polarographic cell, the source of direct voltage, the coupling transformer to the detecting circuit, and the resistance across which the alternating signal is supplied. The source of alternating signal was a Heathkit Audio Oscillator, Model AO-1, which was operated to produce a sine wave at 200 c.p.s. The output of this was about 4.1 volts under normal load, and was fed directly to the horizontal input of the oscilloscope and through a resistor to the synchronizing terminal. The signal for the cell circuit was tapped from a 10,000-ohm linear carbon volume control across the oscillator output, and applied across one of a selection of small resistors in the cell circuit.

Direct voltage was supplied by a Fisher Elecdropode manual polarograph modified in two respects. In parallel with the 100-ohm "STD" control a 400-ohm control was added, with considerable gain in convenience in setting the slidewire span voltage. The main voltage divider was replaced by a 10-turn, 200-ohm Helipot potentiometer, Model A. The Model W Duodial used with this was marked to 1 mv., and could be read to 0.5 mv. without difficulty.

The alternating signal was detected by a filament transformer operated

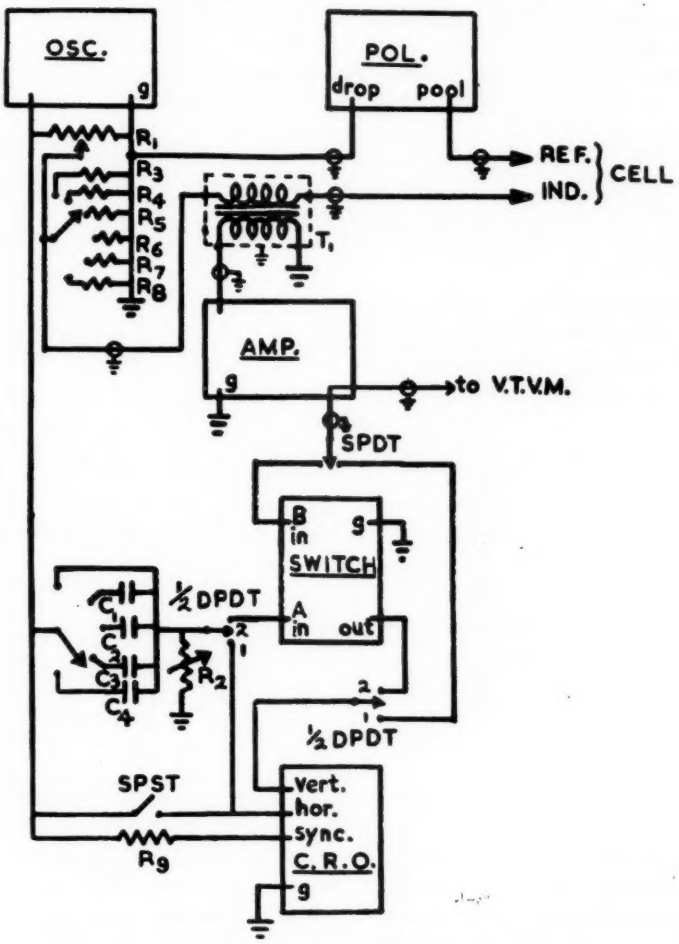

FIG. 1. Circuit diagram.

R_1 10,000-ohm linear carbon
R_2 500,000-ohm carbon
R_3 to R_8 7 to 400 ohm
R_9 470,000-ohm
C_1 to C_4 10 μf. to 0.015 μf.
T_1 Hammond 167 B 25 (6.3: 110)

backward, and was fed to a 6-watt amplifier built in the Department of Physics, University of Toronto. A 500-ohm output was used, and, at full gain with bass boost on, the gain was 700 for a 200-cycle signal. The noise level was 0.2 mv. at full gain, and there was no distortion of a sine wave up to 135 v. output. The cell signal and a reference signal were presented to the oscilloscope through a DuMont Electronic Switch, Model 185. The signals were observed on a Heathkit 5-in. oscilloscope, Model O-7, operated on its 400-v. range at very low vertical gain, to produce a trace as free from noise and visible tran-

sients as possible. Many leads were shielded, as shown, to prevent pickup of stray signals.

To observe the summit potential phenomenon described by Delahay and Adams (2), a Hewlett-Packard A.C. Vacuum Tube Voltmeter was connected as shown, and operated on its 3-v. range.

The characteristics of the components used led to the choice of the following operating conditions: (*i*) a high switching speed, with the pattern appearing as a line, (*ii*) relatively high gain on the amplifier before the switch, (*iii*) lowest possible gain in the switch and oscilloscope, (*iv*) low intensity setting to minimize halo.

Method of operation.—With the cell operating, the oscilloscope, electronic switch, and signal generator were turned on. This gave a pattern shown in Fig. 2*a*. This was adjusted by means of the "A" gain of the switch and the

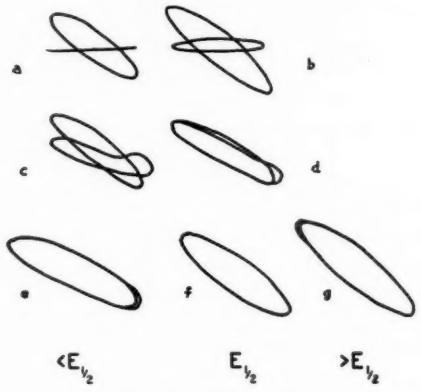

FIG. 2. Oscilloscopic traces.

horizontal gain of the oscilloscope to a suitable size, the phase-shifting resistance having first been set to tilt the figure at about 45°. Next, the amplifier and polarograph were turned on with the applied potential set at zero (Fig. 2*b*). The height of the cell signal was set by the "B" gain of the switch and the amplifier gain to a somewhat lower level. While observing the screen, the potential was increased until a point was reached at which the cell figure became elliptical (Fig. 2*c*). The phase-shifting circuit was used to place the reference signal at the same angle as the cell signal, and the balance and gain controls of the switch were used to superimpose the figures if desired (Fig. 2*d*). Then a short potential interval was investigated with the polarograph until the point of no deviation of the two ellipses was found. By using the sweep generator of the oscilloscope, two sine waves could be matched in the same way. It will be noted that the circuit provides for elimination of the electronic switch so that a single sine wave or ellipse can be projected if desired.

Measured half-wave potentials.—The following observations were made for solutions for which known half-wave potentials were available for comparison.

Solution	Supporting electrolyte	$E_{\frac{1}{2}}$ vs. N.C.E., volts Observed	Literature
0.001 *M* $CdSO_4$	0.1 *M* KCl	−0.661	−0.63 (3)
0.001 *M* $Cu(ClO_4)_2$	0.1 *M* KCl	−0.029	−0.03 (3)
0.001 *M* $Pb(NO_3)_2$	0.1 *M* KNO_3	−0.432	−0.46 (3)
			−0.43 (6)

In each case the reading was checked by resetting the potential dial several times. For cadmium there was found to be an interval of 4 mv. in which no distortion was visible, the middle of which could easily be located to 1 mv. For copper and lead the region of no distortion was about 10 mv. Bubbling with nitrogen for a period of two hours did not change the indication obtained for a fresh solution of cadmium ion.

We do not doubt that the details of this circuit could be improved; for instance, the use of a double-gun oscilloscope would obviate the electronic switch. The principal difficulty encountered was the elimination of stray noise, and it must be stressed that adequate shielding and grounding of the circuit are imperative for satisfactory operation.

We are greatly indebted to Professor J. M. Anderson of the Department of Physics, University of Toronto, for the loan of equipment and for much help with the design of the circuit. We also gratefully acknowledge financial assistance from the University's Advisory Committee on Scientific Research.

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THE FORMATION OF MOLECULAR COMPLEXES BETWEEN SOLID UREA AND *n*-OCTANE VAPOR

By H. G. McAdie[1] and G. B. Frost

The formation of molecular complexes, called adducts, between urea and *n*-paraffins has been known for some time. Schlenk (3) has given a detailed account of their preparation from solution, and has reported an elucidation of their structure on the basis of X-ray evidence. He showed that when straight chain hydrocarbon molecules are added to a concentrated solution of urea, in a suitable solvent, crystallization of the urea occurs in such a way that each hydrocarbon molecule becomes imprisoned in a canal formed by a hexagonal arrangement of urea molecules, as contrasted with the normal closely packed

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tetragonal lattice of urea. The hexagonal structure has now been worked out in detail (4) and the whole subject of urea adducts has been reviewed elsewhere (1, 5).

Schlenk (3) has also reported the slow formation of urea adducts by the mere contact of finely divided tetragonal urea crystals with certain pure liquid *n*-paraffins, and has also suggested the possibility of forming such adducts by exposure of tetragonal urea to the vapor of the lower boiling *n*-paraffins. Redlich and co-workers (2) have reported measurements of equilibrium pressures for various systems consisting of adduct, solid urea, and a long chain molecule. These measurements imply a reversibility between the reactions involving adduct decomposition and formation.

The present work was undertaken in an attempt to throw light upon the mechanism of this reaction between tetragonal urea and pure *n*-paraffin vapors, which is an interesting one from the standpoint of the molecular forces involved. The following is a report of some preliminary experimental findings, and an indication of some of the experimental work in progress.

Reagent grade urea was recrystallized, dried, and screened, the "through 60 mesh on 80 mesh" portion being used. Small samples (40 mgm.) were contained in a basket of 100-mesh copper gauze and suspended on a quartz spiral balance. The balance case was connected with the usual vacuum system and means were provided for the exposure of the suspended sample to *n*-octane vapor at its saturation vapor pressure at 25° C. Provision was also made for the addition of other gases.

On exposure of urea samples, prepared in this way, to *n*-octane vapor, no evidence of adduct formation was observed after 24 hr. It was found, however, that adduct formation took place rapidly in the presence of water vapor, and that if the adducts so formed were decomposed under vacuum, addition of *n*-octane vapor then occurred rapidly in the absence of water vapor, and that cycles of decomposition and absorption of hydrocarbon could be carried out. Adduct formation in the presence of water vapor has been confirmed by X-ray diffraction, the line patterns being identical with those obtained for adducts of several normal hydrocarbons and alcohols prepared from saturated solutions of urea in methanol. The nature of the products formed by the addition of *n*-octane vapor after the evacuation of the adduct and in the absence of water vapor has not as yet been definitely established.

The results of a typical experiment are shown in Fig. 1 where the weight increase, as obtained by readings of spiral extension, is plotted against the square root of the time in minutes. In this experiment, the urea sample was evacuated at 10^{-4} mm. and 25° C. for 24 hr., in order to remove traces of water vapor. It was then exposed to *n*-octane vapor at its saturation vapor pressure at 25° C. for 24 hr. No significant change in weight was observed during this period. Water vapor at a pressure of approximately 11 mm. was then admitted. The sample started to increase in weight immediately, and a gradual swelling occurred. Zero time in Fig. 1 is taken as the time of admission of water vapor.

When the reaction appeared to be approaching completion, vacuum was applied and the weight of the sample decreased rapidly to its initial value.

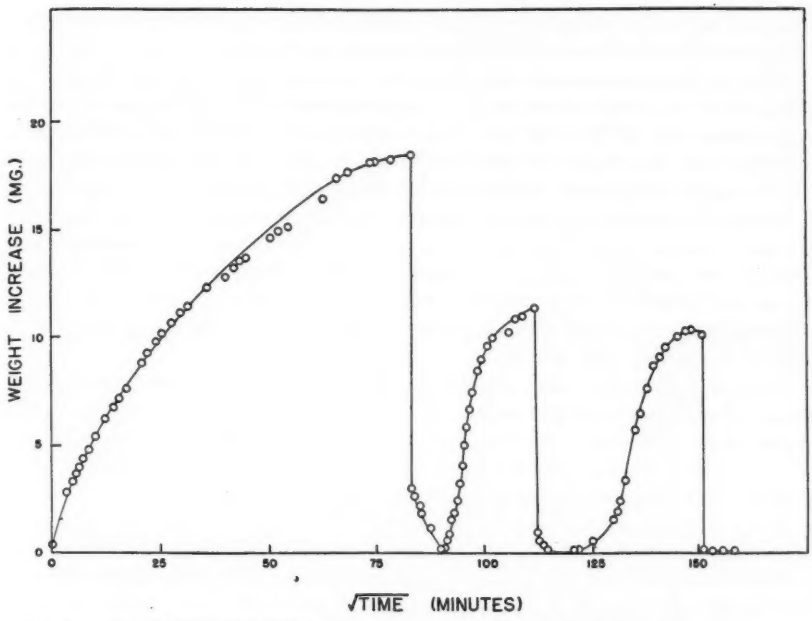

FIG. 1. Typical formation and decomposition curves for the urea–*n*-octane adduct.

Pure *n*-octane vapor at its saturation pressure was then admitted, but no water vapor. A rapid increase in weight occurred (the second rise shown in Fig. 1), the rate decreasing at a much lower uptake of the hydrocarbon. The reaction was allowed to proceed for a time and the cycle of operations repeated. Uptake of *n*-octane was again observed.

If adduct formation occurs during the second and third exposures, some stability of the hexagonal lattice after the withdrawal of the hydrocarbon chain may be indicated. It is also possible that the removal of the hydrocarbon at very low pressure may result in the collapse of the hexagonal lattice into an assembly of microcrystals of tetragonal urea, and that adduct formation takes place more readily on this material of high surface area. It is also possible that the observed uptake of *n*-octane in the absence of water vapor is due to adsorption. Experiments are being carried out with the purpose of deciding among these alternatives.

Adduct formation in the presence of water vapor was accompanied by a marked swelling of the sample. This is probably due to the increased volume of the hexagonal channel structure over the normal tetragonal crystals and has been reported by others (1). It is interesting to note that this swollen state persisted after the decomposition of the sample at low pressure.

While extensive quantitative results are not yet available, the rate of adduct formation appears to have a linear dependence on water vapor pressure over the range from 8 to 15 mm. There appears to be a lower limit of water vapor

pressure (approximately 7 mm.) below which adduct formation does not occur for crystals of the dimensions used in these experiments.

The reaction between urea crystals and *n*-octane vapor in the presence of water vapor was also observed by a photomicrographic technique. At water vapor pressures of 14 to 15 mm. the reaction was observed to proceed quite readily. This was shown by the loss of transparency of the urea crystal and the formation of a fuzzy, opaque, somewhat larger crystal.

Photomicrographic evidence appears to indicate that not all the urea crystals react at once. However, once initiation of reaction occurs on a given crystal, the reaction progresses rapidly through that crystal. When water vapor was present to the extent of 7 to 8 mm. no reaction occurred after 24 hr., indicating again the presence of a limiting water vapor pressure below which adduct formation does not occur.

The fact that water vapor promoted the adduct formation led to an investigation of other possible promoters. Methanol and ethanol, at pressures in the region of 10 to 15 mm., promoted the reaction after considerable time. There is some indication that nitromethane and ethylenediamine behave in a similar manner. The effect of other substances is being studied.

Work is being carried out on the adsorption of water vapor on urea, the determination of the change in surface area on removal of hydrocarbons at low pressure, and more extensive utilization is being made of X-ray techniques. The results will be reported in a subsequent paper.

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1-ALKYL-2-IMIDAZOLIDINETHIONES[1]

BY G. D. THORN[2]

For the study in this laboratory of the fungicidal activity of compounds containing the thiocarbamoyl grouping, it became necessary to have a series of 1-alkyl-2-imidazolidinethiones. Except for a paper by Rich and Horsfall (10) in which is reported the fungitoxicity of *n*-octyl-, *t*-octyl-, and *n*-octadecylethylenethiourea (for which no physical characteristics are given), no reference to simple 1-alkyl-2-imidazolidinethiones is to be found in the literature.

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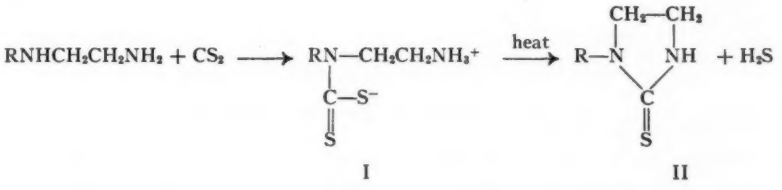
The reaction of equimolar amounts of ethylenediamine and carbon disulphide was shown by Hofmann (4) to yield N-(β-aminoethyl)dithiocarbamic acid (I, R = H). Thermal decomposition of this inner salt gave 2-imidazolidinethione (II, R = H). These reactions were later extended to various N- and N,N′-substituted 2-imidazolidinethiones by van Alphen (1), Baum (2), Donia, Shotton, Bentz, and Smith (3), Hurwitz and Auten (5), Lob (7), Newmann (8), Schmidt (11), Vaugh and Bean (12), and Zienty (13).

Following the classical procedures, a series of 1-alkyl-2-imidazolidinethiones has been prepared.



I II

EXPERIMENTAL[3]

The N-alkylethylenediamines were prepared either by reaction of the requisite alkylamine with 2-bromoethylamine (9) (R = ethyl through hexyl), or by reaction of an alkyl halide with 98% ethylenediamine (6) (R = heptyl through dodecyl).

The N-alkyl-2-imidazolidinethiones were prepared essentially according to the method given by Donia *et al.* (3). The reaction of the amine with carbon disulphide was carried out in ether to give a fine white precipitate of the dithiocarbamic acid inner salt. The use of acetone (3) as the reaction medium resulted in yellow gummy precipitates, which could however be triturated with ether to give more tractable material.

A typical preparation is described, in which the alkyl group is octyl: A solution of 10.1 gm. (0.059 mole) of N-octylethylenediamine in 80 ml. ether was cooled to 10° C. in an ice-bath, and stirred vigorously while 4.72 gm. (0.062 mole) of carbon disulphide in 30 ml. ether was added dropwise. Stirring was continued for 30 min. after addition was completed. The precipitate was removed by filtration, washed with ether, and air-dried. The yield was 14.3 gm. (98%). Found: N, 11.2%. Calc. for $C_{11}H_{24}N_2S_2$: N, 11.3%.

The inner salt was heated for two hours in a wide-mouthed Erlenmeyer flask immersed in an oil bath at 130° C. The dark residue was crystallized from hexane to give 9.7 gm. (77%) of 1-octyl-2-imidazolidinethione. The material was then recrystallized from hexane to constant melting point (Table I).

The yields given in Table I are calculated from the amount of material obtained after one crystallization of the crude imidazolidinethione. Hexane was the preferred solvent for recrystallization, except for the first three members of the series, where ether or hexane–acetone was used.

[3]*All melting points are uncorrected and were obtained on the Fisher-Johns block.*

TABLE I

1-ALKYL-2-IMIDAZOLIDINETHIONES

R in formula II	Yield, %, from I	m.p., °C.	Analyses			
			Found		Calc.	
			C	H	C	H
Ethyl	72	79–80	46.1	7.56	46.2	7.69
Butyl	70	78–79	53.3	8.87	53.2	8.87
Pentyl	81	68–68.5	55.8	9.35	55.8	9.30
Hexyl	90	71–72	57.9	9.57	58.1	9.68
Heptyl	81	69–70	60.0	10.15	60.0	10.00
Octyl	77	52–53	61.7	10.36	61.7	10.28
Nonyl	73	56–57	63.2	10.38	63.2	10.53
Decyl	81	64.5–65	65.0	10.38	64.5	10.74
Dodecyl	74	60–61	66.9	10.91	66.8	11.10

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